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THE IN-PLACE POLLUTANTS PROGRAM

BACKGROUND AND THEORETICAL CONCEPTS

- VOLUME II

MARCH, 1987

Ministry of the Environment
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J. Bishop, Director
Water Resources Branch

IN-PLACE POLLUTANTS PROGRAM - VOLUME II

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PREFACE

The In-Place Pollutants Program addresses the impact of contaminants in sediment on overlying water quality and aquatic biota with the aim of developing strategies for the management of contaminated sediments.

This report, Volume II, provides the background and an overview of the theoretical concepts related to the program and companion volumes will provide the following:

Volume I: In-Place Pollutants Program - A Program Overview. (expected March, 1987).

Volume III: Phase 1 Studies. (expected April, 1987).

Volume IV: Phase 1 Data Summary. (expected April, 1987)

Subsequent studies will be reported in other volumes in the series.

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CHAPTER I - INTRODUCTION

1.1 BACKGROUND

The study of in-place pollutants, defined as inorganic and organic contaminants in sediment, is designed to increase our knowledge of the influence of contaminants in bottom sediment on the aquatic ecosystem.

The concept of contaminated sediment as a potential source of pollutants grew out of findings from sediment studies associated mainly with dredging. During the early 1970's, the need to control contaminants in dredged sediments became apparent as a result of studies that identified the absence of certain benthic indicator species in harbours with contaminated sediments (Persaud and Wilkins, 1976). These early studies did not establish specific biological impacts of contaminants in sediments on aquatic biota but identified that certain elevated levels of contaminants were associated with the absence of certain benthic indicator species. The results from this early work were used in the development of a set of bulk chemical guidelines for evaluating dredged material for open-water disposal (Persaud and Wilkins, 1976). The guidelines are also used to evaluate sediment quality during routine surveillance and monitoring studies.

The bulk chemical guidelines, developed mainly for metals, nutrients, PCB's and oil and grease, address the 'total' amounts of the respective chemical present in a given sediment sample. This approach may be used for basic guidance in environmental protection but is not totally satisfactory for assessing the biological significance of contaminants in sediment, especially the heavy metals of which only a fraction of the total may be bioavailable or can be released to the water column. Appropriate procedures had to be developed to properly address the significance of contaminated sediments with respect to the organisms inhabiting the aquatic ecosystem.

The main issues in this regard relate to:

- the potential release of contaminants in sediment to the overlying water
- the toxic (lethal and sublethal) effects on bottom-dwelling (benthic) organisms
- the uptake (bioaccumulation) of contaminants from sediments by benthic organisms.

1.2 THE ORIGIN AND SIGNIFICANCE OF IN-PLACE POLLUTANTS

Contaminants that enter the aquatic environment may exist as distinct entities, dissolved in water or attached to particulate matter depending on the physical and chemical properties of the contaminants. Much of the dissolved contaminants that are not volatilized to the atmosphere are taken up by aquatic plants and animals or precipitate out of solution and become incorporated in bottom sediments.

Most chlorinated hydrocarbons and metals have a strong affinity for particulate matter such as fine-grained sediment (silt/clay), organic detritus and algae. As a result, these contaminants adsorb onto particulates in the water column and eventually settle with the particulates to the bottom.

The particulates act as 'scavengers' or 'carrier particles' in removing contaminants from the water column and concentrating them in bottom sediments which become a 'sink' for a variety of contaminants. Because bottom sediment acts as a sink and changes very slowly, it makes a very good medium for monitoring historical trends and sources of pollution.

It was previously thought that, once contaminants enter the sediment, they are effectively 'locked-up' from the rest of the ecosystem. Evidence (Zepp, 1978), however, indicates that sorption of contaminants to sediment is a reversible process and contaminated sediments may be a continual source of contaminants to water and fish after external inputs (point and non-point sources of contaminants) have ceased. Field and laboratory studies (Eadie et al., 1982, Meier and Rediske, 1984)

suggest benthic organisms can take up and concentrate contaminants directly from sediments.

The significance of in-place pollutants has been identified in a report by the International Joint Commission (IJC, 1985) on Great Lakes Water Quality where it was pointed out that 38 of the 42 areas of concern around the Great Lakes have moderately to heavily contaminated sediments and these in-place pollutants are considered to be the most common sources of continuing water quality problems. (IJC, 1985). Although harbours, because of their generally poor hydrodynamic characteristics (lack of currents and barriers to water movement), present ideal situations for the accumulation of contaminants in sediments (in-place pollutants), other nearshore 'depositional' areas, such as embayments are also found to have highly contaminated sediments (Persaud et al., 1985).

1.3 THE IN-PLACE POLLUTANTS PROGRAM

The MOE In-Place Pollutants Program began in 1983 and was designed to initially provide the necessary basis, through field studies, to understand how contaminated sediments affect water quality, benthic macroinvertebrates and bottom feeding fish. With a basic understanding of in-place pollutants established, efforts are being directed towards defining the mechanisms of contaminant uptake by organisms, the sublethal effects of contaminants on organisms and factors affecting the movement and fate of contaminants in sediments. The information gatherered through such studies would provide guidance on improving bulk chemical guidelines to reflect the biological significance of contaminants in sediment and to establish guidelines for additional parameters of concern.

The Program initially focused on two major groups of chemicals; the heavy metals and the organochlorine compounds (PCB and selected pesticides). This narrow group of contaminants was selected because it is extremely difficult, under field conditions, to isolate the biological impacts of specific contaminants from the heterogeneous mass of chemical substances that may exist in sediment. Sediment

bioassessment procedures using laboratory microcosms are also being developed to provide the basis for examining the toxic or bioaccumulative aspects of specific chemicals or groups of chemicals on aquatic biota.

The Program design has also taken into account the uneven distribution of contaminants in sediment within and between geographical locations (Namminga and Wilhm 1977; Glooschenko et al, 1981; Persaud et al, 1985). The initial phase of the program involved data collection from various locations of the lower Great Lakes and the interconnecting channels. This provided indications of how different sediment types and degree of contamination may affect the indigenous benthic population. Current in-place pollutant investigations are carried on in an intensive fashion in fewer geographical areas.

The information obtained from the In-Place Pollutants Program will provide the scientific basis for developing strategies for the management of contaminated sediments. The objectives of this program are outlined below. A comprehensive overview of the Program is outlined in another report, Program Summary, Volume I.

1.3.1 Program Objectives

The objective of the In-Place Pollutants Program is:

to determine the potential impacts of contaminants in sediments on overlying water quality and on aquatic biota and to develop strategies for the management of contaminated sediments that will ensure the protection of water quality and water uses. This will involve the investigation of bottom water chemistry, sediment chemistry, fate and transport of sediments and associated contaminants, toxicity of contaminated sediments to biota and the bioaccumlation potential of contaminants in sediments.

To achieve this objective, the following tasks are being undertaken:

1. Characterize sediment type and chemistry in areas of known sediment contamination in Ontario.

2. Determine the fate of contaminants in sediments by assessing the physical transport of sediments into and out of selected areas.

3. Evaluate the toxicity of contaminated sediments to aquatic biota that are representative of those found in Ontario's aquatic environment through the use of in-situ and laboratory testing.

4. Evaluate the bioaccumulation of contaminants from sediments in biota and determine the mechanism of transport of contaminants from sediments into biota.

5. Determine the mechanism of transport of contaminants from sediments into the water column and biota.

The remaining sections of this volume provide an overview of relevant background information on the sources and properties of metals and organic contaminants in the aquatic system and their influence on benthic organisms. Certain terms will be used in the text of this report and the definitions are as follows:

Bioaccumulation - Uptake and retention of environmental substances by aquatic organisms from both the environment (water, sediment) and food.

Bioconcentration Factor - The ratio of the measured residue in the biota compared to the residue of the substance in the ambient air, water or sediment environment of the organism.

Biomagnification - The magnification (increase in concentration) of an environmental substance through the food chain.

CHAPTER II - THEORETICAL CONCEPTS - AN OVERVIEW

2.1 SOURCES AND PROPERTIES OF METALS IN THE AQUATIC ENVIRONMENT

The metals of environmental concern are those normally referred to as trace metals or heavy metals. These terms are often used interchangeably. Heavy metals can be defined as those metals with a density greater than 5 gcm^{-3} (Hakanson and Jansson, 1983), or specific gravity of over 4.5 (Jarvis, 1983). Trace metals are regarded as those found in small concentrations in biological systems and may be essential to life (Forstner and Wittman, 1981).

Organisms have a wide range of tolerance for some metals such as copper, iron, manganese and zinc while exhibiting a narrow tolerance range for others such as mercury and lead. For the purposes of this report the metals of interest are the heavy metals with known toxic properties and include cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), mercury (Hg), nickel (Ni) and zinc (Zn). Iron (Fe) and manganese (Mn) have been included because of their important influence on the fate of other metals in the aquatic environment.

Arsenic which is a metalloid (exhibiting properties of both metals and non-metals) has also been included among the heavy metals considered in this study. Of the metals listed above, lead, cadmium, mercury and arsenic are of major concern from an ecosystem 'health' perspective.

Heavy metals in sediments are derived primarily from natural sources (termed lithogenic or geochemical sources) and man-made sources such as industrial or mining processes (referred to as anthropogenic sources). In most cases certain forms (those available to aquatic life) in which a metal exists in the environment are of greater importance from a toxicological point of view than the total concentrations of the metal.

2.1.1 Lithogenic Sources of Metals

The primary source of heavy metals is rock. Rock that is exposed at or just below the earth's surface undergoes physical and chemical weathering which transforms the rock into small mineral fragments which make up the inorganic component of soil.

The breakdown of rock results in the release of many metals which are of a size that can be easily transported by water. The heavy metal concentration in a given soil will therefore be a reflection of the chemical composition of the parent rock material from which the soil was derived providing there are no major anthropogenic additions.

When water and soils interact the soil minerals may undergo further chemical transformations that release individual heavy metals which can then be transported and deposited great distances from their origin. Water and sediment in areas of metal-bearing bedrock will also contain relatively high levels of those metals present in the bedrock.

2.1.2 Anthropogenic Sources of Metals

The waste products of many metal processing and other chemical industries using metallic compounds can contain significant quantities of heavy metals which find their way into the aquatic environment. Municipal wastes (storm and sanitary discharges) resulting from urban runoff and domestic sewage discharges also contain varying levels of metals. Atmospheric emissions originating from natural sources (e.g. volcanoes) as well as manmade sources (e.g. industries, automobile exhausts) also contribute to the overall loading of various metals to the aquatic environment.

2.1.3 Fate of Metals in the Aquatic Environment

Heavy metals are introduced into the aquatic environment in solid, dissolved or colloidal forms*. The solids include various mineral forms and metals adsorbed onto particulates such as organic matter. The dissolved fraction (defined as that fraction which will pass through a 0.45 μm filter) includes the ionic forms of metals (cations) and metal complexes formed with dissolved organic matter. Metals in the dissolved fraction can be adsorbed onto particulate matter or be taken up by aquatic organisms.

The fate of heavy metals in the aquatic environment is to a great extent governed by the physicochemical conditions of the environment. The three important conditions are Eh, pH and availability of sorbing materials.

Eh or redox potential is a measure of the concentration of electrons in a medium (a positive Eh value is indicative of an oxidizing environment - presence of free or dissolved oxygen while a negative value suggests a reducing environment - absence of oxygen). pH is a measure of the hydrogen ion (H^+) concentration (acidity or alkalinity) in a given solution.

The sorbing agents of metals in the aquatic environment include minerals such as clays, organic detritus, algae and the hydrous oxides of iron and manganese. Metals may also be coprecipitated with hydrous iron, manganese oxides and iron sulphides. Metals that are adsorbed onto or coprecipitated with particulate matter eventually settle to the bottom of water courses and become incorporated in sediments.

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* Colloids range in size from 10^{-4} μm to 1 μm. A small volume can adsorb large quantities of metals because of the large surface area to volume ratio and an overall negative charge.

2.1.4 Mechanisms of Sediment - Metal Association

Metals derived from natural sources, such as the weathering of bedrock, may to a large extent exist in the mineral forms of the clay-sized sediment fraction. The term clay is used to denote the physical size. For example, clay refers to particles smaller than 2 µm as opposed to clay minerals which are aluminosilicate minerals occurring in the clay-sized fraction of sediments. The clays, by virtue of the presence of these metallic clay minerals as well as other fine-grained particulates (such as organic material) will contain significantly higher levels of metals as opposed to coarse-grained sediment such as sand which is made up mainly of quartz and feldspars with very low heavy metal contents (Forstner and Wittman, 1981).

Certain metals in fine-grained minerals often occupy positions in the lattice structure of the minerals. The metals in these positions are considered inert in that they are not biologically available. The availability of metals in other types of association with various sediment fractions depends on how tightly the metals are bonded to the sediment and factors such as the Eh and pH of the sediment. The various associations between metals and the different materials making up sediment are referred to as geochemical partitioning. Metals are associated with the sediments by processes such as adsorption, co-precipitation and complexation.

2.1.4.1 Adsorption of Metals

Naturally occurring colloidal material such as the hydrous oxides of iron and manganese, organic matter and clays form ideal substrates for metal adsorption. The surfaces of these materials
are negatively charged and attract the positively charged metal ions (cations) which become adsorbed onto the particulates mainly through electrostatic forces. This type of adsorption is referred to as non-specific adsorption where

the cations attach onto any available site (non-selective). This type of metal-sediment association is referred to as the easily exchangeable or cation exchange phase. There is a continuous exchange of cations between the sorbing agents and the surrounding water.

Some cations can adsorb strongly to particulate matter forming specific chemical bonds. This type of adsorption is referred to as specific adsorption and the cations are not as easily released as in the exchangeable form.

2.1.4.2 Co-precipitation of Metals

The hydrous oxides of iron and manganese can form coatings on mineral surfaces such as clays and as they precipitate, the negative charge on the oxide can attract metals which become incorporated in the lattice of the coating. This is referred to as co-precipitation.

Co-precipitated metals may be residual (derived from natural sources through weathering) or obtained from solution. The ease with which co-precipitated metals are released depends on the nature of the chemical bonding. Freshly precipitated metals can be released with ease but over time the bond strengthens and release becomes more difficult.

Hydrous oxides of iron and manganese are good scavengers of metals under oxidizing conditions such as in the water column but under reducing conditions (absence of oxygen) they may become soluble thus releasing the metals that have bonded to the surface.

Metals in this geochemical phase (hydrous oxides) are referred to as "easily reducible" or "moderately reducible" depending on the ease or difficulty with which they can be released.

2.1.4.3 Complexation of Metals

Metals can form bonds with many natural and synthetic organic compounds, a process known as complexation or metal-organic complex formation. Metals may form bonds of moderate strength by replacing the H^+ on the -COOH and -OH groups of organic acids. Strong bonds are created when metals attach directly to carbon atoms forming organo-metallic compounds. Strong bonds are also formed when metals attach to two or more sites of the organic molecule where the metal is said to be chelated.

Metal-organic complexes can precipitate directly or adsorb onto solids such as clay minerals.

2.1.5 The Influence of Eh and pH on Metal-Sediment Associations

Eh or the oxidation-reduction (redox) potential is a measure of the ability of a medium to accept or supply electrons during chemical (oxidation-reduction) reactions. Oxidation refers to a loss of electrons by a chemical 'agent' (electron donor) and reduction is a gain of electrons by another agent (receptor). For example, when hydrogen and oxygen combine to form water ($2H_2 + O_2 \longrightarrow 2H_2O$) the hydrogen is oxidized (loss of electrons) by the oxidizing agent (oxygen). In the process the oxygen is reduced (gain electrons). Oxygen is the strongest oxidizing agent found in nature.

Eh is usually measured in millivolts and positive values (between 0 and 1000) indicate oxidizing conditions which would for example, exist in an oxygenated water column. Negative values (between 0 and - 1000) are indicative of reducing conditions such as highly organic bottom sediments where the lack of oxygen creates anaerobic conditions.

The Eh of a medium greatly influences chemical reactions involving iron and manganese oxides which have a great bearing on the fate of

heavy metals in the aquatic environment. As an example, under oxidizing conditions, such as in the upper water column, heavy metals will coprecipitate with sedimenting materials whereas in a reducing environment, such as anaerobic bottom sediments, the metals may be released as a result of dissolution of the iron and manganese oxyhydroxides. In general, lower redox potentials will favour the soluble forms of iron and manganese (Fe^{++} and Mn^{++}).

It must be pointed out that a low or negative Eh potential only suggests a reducing potential in a medium. The actual reduction will depend on the presence of reducing agents in the medium.

Much of the chemical reduction in bottom sediments will normally occur in the area bordering the sediment-water interface where organic matter containing many reducing materials accumulates. As sediment becomes buried by new material, it is likely that further reactions will occur only slowly in the buried material.

pH is a measure of the hydrogen ion (H^+) content of a solution. The pH scale ranges from 0 to 14 where 7.0 is neutral pH and values less than seven indicate acidic conditions (the lower the value the stronger the acid) while values greater than seven indicate alkaline conditions. pH is a very important factor in the dissolution of minerals and ion exchange reactions. At low pH values the H^+ in the medium will compete effectively with metal cations for adsorption sites on particulates thus reducing the capacity of the particulates to 'scavenge' metals from solution. pH also controls the strength of bonds in the formation of organic-metal complexes.

Eh and pH are closely interrelated and a change in one usually results in a change in the other. Although they are not the only factors controlling the fate of metals in the aquatic environment, they regulate a variety of the other processes occurring within the sediment-metal environment. In order to gain a good understanding of the influence of Eh and pH on the behaviour of specific metals, an Eh - pH diagram is usually constructed and a variety of chemical

information is summarized in the diagram. Examples of these can be found in the work of Krauskopf (1979).

2.1.6 Metal-Organic Carbon Relationships

Organic carbon, normally measured as total organic carbon (% TOC) provides an indication of the organic matter content of sediment. Organic matter from natural sources is derived mainly from animal and plant remains which are broken down by microcrganisms. The most prevalent type of end products are compounds referred to as humic and fulvic acids. A variety of synthetic organic materials are also introduced into the aquatic environment via municipal and industrial discharges.

Organic carbon is very important in the formation of metal- organic complexes which remove metals from solution. In many instances a very strong positive correlation exists between % TOC and metal concentrations in sediments implying close metal-organic matter relationships. In the presence of high concentrations of minerals such as clay, no correlation or a negative correlation between metals and % TOC may exist. The most plausible explanation for this is that in the presence of high mineral content, dissolved organic matter is preferentially adsorbed onto the minerals effectively diminishing the metal-organic association (Jackson et al., 1978).

2.1.7 Sources and Properties of Toxic Heavy Metals

Arsenic: Arsenic is considered a metalloid (or semi-metal) which is defined as an element having both metallic and non-metallic properties. The major anthropogenic sources of arsenic include pesticides, coal and petroleum, mining operations and detergents. The major natural source is weathering.

Much of the arsenic introduced to the aquatic environment becomes bound up in the sediment, although it is quite mobile and can also be found in biota and water (Callahan, et al., 1979). The fate of arsenic is heavily dependent on the Eh and pH of the environment. It has been suggested that co-precipitation with, and adsorption to the hydrous oxides of iron and manganese are the principal mechanisms of removal of dissolved arsenic from the water column (Callahan et al., 1979). Arsenic has a biological half-life of about seven days and can be biologically methylated.

Arsenic is quite toxic to plants and animals and therefore will not bioaccumulate in significant quantities. Bioaccumulation is usually greater at the lower trophic levels with much of the concentration in the lipid content of the organisms compared with other tissues. Fish can accumulate low levels of arsenic from their food and the water column.

Cadmium: Cadmium is rare in nature, occurring mainly in zinc bearing ores. The main sources of cadmium include zinc-bearing ores and metal refining industries. It is used in such processes as electroplating, pigment production and manufacture of batteries.

It is quite mobile in the aquatic environment where it is transported in the ionic states and readily forms complexes with organic matter. Much of the cadmium transported to sediments is through sorption to particulates especially at higher (alkaline) pH levels. The remobilization of cadmium from sediments depends mainly on the stability of its metal-organic complexes. In unpolluted and acidic waters, cadmium will exist mainly in the ionic forms which are readily accumulated by aquatic organisms.

It is highly toxic to plants and animals and there is no evidence of methylation (Callahan et al., 1979). Cadmium may be taken up by aquatic invertebrates from water, sediment and food but uptake is much lower in comparison to other metals. In fish, cadmium may accumulate in organ tissues such as the liver and gut and in the skin and gills (Moore and Ramamoorthy, 1984).

Chromium: Chromium occurs naturally as chromite ore. It is used in the preparation of corrosion resistant metal alloys, refractory bricks for high temperature uses, dyes, and in leather tanning and electroplating industries. Chromium is a biologically essential nutrient.

The chief mechanism of transport to sediment is through adsorption to organic matter and iron and manganese oxides (Moore and Ramamoorthy, 1984).

Chromium can be accumulated in aquatic organisms to levels higher than ambient water but normally lower than sediments. Although very little is known about the biotransformation of chromium, it has been demonstrated that it can be transferred through the food chain to aquatic organisms (Callahan et al., 1979). Toxicity of chromium to aquatic organisms is generally low compared with the toxicity of several other metals such as mercury, cadmium, copper, lead, nickel and zinc (Moore and Ramamoorthy, 1984).

Copper: Copper is widely distributed in nature occurring mainly as copper sulphide mineral. It is a biologically essential trace element. Copper is used mainly in electrical wires, pipe for plumbing and in biocides. In the aquatic environment, copper forms complexes with organic matter, clays and iron and manganese hydrous oxides.

The fate of copper is highly Eh and pH dependent. It has been found that levels of copper are higher in the water column in fall and winter and lower in spring and summer. This has been attributed to higher bioaccumulation during the growing season (Callahan et al., 1979).

Copper is quite toxic to aquatic organisms in the soluble (Cu^{2+}) form. It appears to bioaccumulate in organisms but there is no evidence of food chain biomagnification (Callahan et al., 1979).

Lead: Lead occurs naturally in the elemental form and as a constituent of many minerals. Lead is used in the manufacture of acid storage batteries, ammunition, solders, leaded gasoline (tetraethyl lead) and paint pigments (Moore and Ramamoorthy, 1984).

Soluble lead readily forms complexes with organic matter, inorganic solids and manganese oxides. Lead is quite mobile in acidic waters and can be remobilized from sediments through biomethylation.

Lead has been found to be toxic to fish and invertebrates and inorganic lead can be microbially methylated to tetramethyl lead which is more toxic and can be rapidly bioaccumulated. Although lead can bioaccumulate in certain aquatic organisms, there is no evidence of food chain biomagnification (Moore and Ramamoorthy, 1984).

Mercury: Mercury occurs naturally in low concentrations in many types of rock and can enter the aquatic environment through weathering of rock. Mercury was widely used in pesticides, paints, pharmaceuticals, manufacture of chlorine, medical and dental equipment and batteries (Moore and Ramamoorthy, 1984). Major industrial sources in Ontario e.g. chloralkali plants were virtually eliminated in the early 1970's.

In the aquatic environment, mercury readily adsorbs to inorganic and especially organic particulates. Desorption from sediments is slow and is regulated mainly by Eh and pH (Callahan et al., 1979). Mercury can be remobilized from sediments through biomethylation and become readily available to aquatic life. The organic (methylated) forms of mercury are very toxic and can also bioaccumulate to levels affecting wildlife and humans.

Nickel: Nickel occurs naturally in the earth's crust. Nickel is used in electroplating, battery manufacture, photoengraving and in the manufacture of metal alloys (Moore and Ramamoorthy, 1984). It is one of the most mobile of the heavy metals, sorbs to organic material and coprecipitates with iron and manganese oxides, especially at pH's over 9. At lower pH's, it exists mainly in the soluble forms. In reducing environments, insoluble nickel sulphide precipitates can be formed.

Nickel is generally less toxic than most of the metals (Moore and Ramamoorthy, 1984). Nickel bioaccumulates in very low concentrations (Callahan et al., 1979).

Zinc: Elemental zinc occurs naturally in the earth's crust. Zinc is an essential nutrient. Zinc is used mainly in metallurgical industries for the preparation of alloys.

In the aquatic environment, zinc will adsorb to organic matter, iron and manganese oxides and clay minerals.

Zinc can be bioaccumulated in organisms. There is no evidence that it can be biomethylated and toxicity to aquatic organisms is relatively low compared with other heavy metals such as mercury, copper and cadmium (Callahan et al., 1979).

2.1.8 Assessing the Availability of Heavy Metals from Sediment

Traditionally, sediment assessment is based on measurement of the total concentration of contaminants (bulk chemistry). However, bulk chemistry information does not provide a clear indication of the availability of heavy metals from sediment to the water column or the biota that feed on the sediments.

The availability of heavy metals can be estimated if the quantities of metals in the various geochemical fractions of sediment are known. Various step-wise extraction schemes (selective extraction procedures) have been developed to remove metals from specific geochemical phases. The selective extraction schemes advanced to date are operationally defined by the chemical extractants used. This implies that absolute amounts of metals associated with a particular geochemical fraction may not be released in a given step. However, the schemes do provide good estimates.

The scheme outlined in table 2.1 has been developed for the In-Place Pollutants Program and is based on information published in the literature (Forstner and Wittman, 1981; Jackson et al., 1978; Tessier et al., 1979; Brannon et al., 1976; Gupta and Chen, 1975).

The first step identifies the soluble metals present in the interstitial (pore) water (IW). This fraction is considered to be readily available to the aquatic biota (Forstner and Wittman, 1981).

The second step identifies the weakly adsorbed fraction of metals. This fraction is associated with sediments mainly through physical adsorption. The metals (+ve charge) attach (non-specifically) to negatively charged surfaces of clays and organic particulates. The metals in this phase (F1) are in equilibruium with the water soluble phase (IW).

TABLE 2.1 SELECTIVE EXTRACTION SCHEME

STEP	PHASE	EXTRACTANTS
1	Interstitial water (IW)	Centrifuge at 15,000 rpm/10 min.
2	Weakly adsorbed and cation exchangeable (F1)	1M NH_4OAC (ammonium acetate)
3	Specifically adsorbed and easily reducible (F2)	0.1M $NH_2OH.HCl/HNO_3$ (Hydroxylamine hydrochloride,(pH 2)
4	Organic Complex (F3)	30% H_2O_2 + HNO_3 + NH_4OAC (pH 2) (Acidified hydrogen peroxide, followed by NH_4OAC extraction) at 95°C.
5	Coprecipitates (F4) (reducible Fe/Mn hydroxides)	1.0M $NH_2OH.HCl/HOAC$ (25% V.V) at 95°C
6	Residual (F5)	HNO_3:$HClO_4$ (2:1, V:V) at 150°C.

Step three examines the specifically adsorbed (chemical adsorption) and easily reducible fraction (F2). The specifically adsorbed metals differ from those in phase F1 in that the association is stronger than mere electrostatic adsorption. The metals form weak bonds with the solids. The chemical extractants used in this step selectively dissolve the manganese oxides while having little effect on the iron oxides. Release in the natural environment can be triggered under reducing (anaerobic) conditions.

The fourth step releases the metals associated with organic complexes and sulphide compounds (F3). In the natural environment metals from sulphides can be released under oxidizing conditions (change in redox potential). Organic matter can be degraded under oxidizing conditions, releasing metals (Jackson et al., 1978).

The fifth step identifies the metals sorbed to iron and manganese oxides (F4). These oxides can exist as nodules, concretions or coatings on particulates. They are good scavengers of metals but are unstable under anaerobic conditions (low Eh) (Jackson et al., 1978).

The sixth step identifies the residual phase (F5). The metals in this phase are 'inertly' bound within the crystal lattice of minerals and are normally unavailable in the sedimentary environment.

2.2 SOURCES AND PROPERTIES OF PCB's AND ORGANOCHLORINE PESTICIDES IN THE AQUATIC ENVIRONMENT

The organochlorine compounds (OC) selected for this study are the group routinely analyzed in a PCB-OC Scan. These include polychlorinated biphenyls (PCB's); the cyclodiene pesticides-aldrin, dieldrin, endrin, endosulfan, chlordane, heptachlor and mirex; hexachlorobenzene; DDT and its metabolites DDD and DDE and the methoxy analogue of DDT, methoxychlor.

Unlike the heavy metals which can be derived from natural sources, the organochlorine compounds listed above are synthetically derived and enter the aquatic environment through industrial, agricultural and domestic uses and in some cases, deposition from the atmosphere. Many of these compounds are extremely persistent (long-lived) and have a high affinity for particulate matter. They are often transported to lake and river sediment where some, notably DDT, PCB, mirex, endosulfan and dieldrin, persist for many years.

In addition to sorption onto particulate matter, there are a variety of other processes governing the fate of organochlorine compounds in the aquatic environment. Some compounds can be volatilized from surface waters to the atmosphere while the process of photolysis (degradation by sunlight) can degrade certain compounds. Because of the lipophilic (fat soluble) nature of many organochlorines and their low solubility in water, many of them will be preferentially taken up in the lipid pool (fatty tissue) of aquatic organisms. Organisms are capable of breaking down (metabolize) certain compounds but if the rate of degradation is less than the rate at which the organism is accumulating the compound, it may bioaccumulate in the organisms. The metabolic breakdown of biodegradable compounds often results in products (metabolites) that exhibit different physical and chemical properties from the parent compound.

Compounds that bioaccumulate can be transferred through the food chain with organisms in each of the higher trophic levels showing higher concentrations - a process referred to as biomagnification. Notable examples of compounds that are biomagnified are DDT and PCB's. These substances can accumulate in fish to levels that have necessitated the publication of Fish Consumption Advisories (MOE and MNR, 1986) and as well, the establishment of criteria to protect fish eating birds (IJC, 1977).

Many of the organochlorine compounds are not acutely toxic to aquatic organisms but may result in subtle physiological changes that remain unnoticed until they become chronic. The subtle effects may result in genetic or reproductive changes that can substantially alter the numbers or types of organisms inhabiting a particular environment.

2.2.1 Environmental Properties of PCB's and Organochlorine Pesticides

Aldrin, Dieldrin and Endrin

Aldrin, ($C_{12}H_8Cl_6$) is an organochlorine insecticide that when applied to the environment, rapidly volatilizes or is readily converted to its epoxide, dieldrin ($C_{12}H_8Cl_6O$). Because aldrin is quickly converted to dieldrin, aldrin is not readily bioaccumulated by aquatic biota. Dieldrin is very persistent in the environment. It bioaccumulates in animal tissues from which it is eliminated very slowly. It is a very effective insecticide against termites and residues resulting from soil application of aldrin are insecticidal for several years. Aldrin and dieldrin have not been used in substantial amounts in Ontario for several years. Dieldrin can be oxidized to its stereo-isomer (endo-endo isomer) endrin. Endrin ($C_{12}H_8Cl_6O$), was an insecticide applied to the soil but has not been used since the late 1960's. It is environmentally very persistent, may be bioaccumulated by aquatic biota and is very toxic to fish (McEwen and Stephenson, 1979) and mammals (Worthing, 1983).

Endosulfan (I and II) and Endosulfan Sulphate

Endosulfan ($C_9H_6Cl_6O_3S$) is currently used as an insecticide for vegetable production in Ontario. It consists of a mixture of two isomers - alpha endosulfan or endosulfan I (making up about 70% of technical endosulfan) and beta endosulfan or endosulfan II (comprising about 30% of technical endosulfan). Endosulfan is only slightly soluble in water, very soluble in organic solvents, but does not bioaccumulate in significant amounts. The beta-isomer can persist for over a year. Both isomers can be oxidized to endosulfan sulphate, ($C_9H_6Cl_6O_4S$) the major metabolite which is very toxic to fish (McEwen and Stephenson, 1979).

Heptachlor ($C_{10}H_5Cl_7$) is an insecticide also known as heptachlorodicyclo-pentadiene but has not been used since the mid 1960's. In the aquatic environment it will undergo rapid hydrolysis. Portions that are not hydrolyzed will bioaccumulate (Callahan et al., 1979). It is a very persistent insecticide with significant potential for biomagnification. Heptachlor may be highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Heptachlor epoxide ($C_{10}H_5Cl_7O$) is a metabolite of heptachlor. It is highly persistent in the environment (being resistant to biological or chemical transformation) and very toxic to aquatic biota (Pers. Comm. N. Bazinet).

Mirex ($C_{10}Cl_{12}$) is an insecticide that was used in the Southern U.S.A. for the control of fire ants. Mirex was manufactured until the mid-1970's on the U.S. side of the Niagara River. Significant impacts in Ontario are limited primarily to Lake Ontario from U.S.A. sources. It was also used as a flame retardant agent under the name of dechlorane. Mirex is extremely persistent, insoluble in water and readily bioaccumulates in organisms since it is lipophilic.

Chlordane ($C_{10}H_6Cl_8$) an insecticide applied to soil, is made up of primarily alpha and gamma chlordane. The use of chlordane has been

discontinued in Ontario except for termite and carpenter ant control. It is fairly insoluble in water and soluble in most organic solvents. There is no evidence of bioaccumulation. It is very persistent in soil (McEwen and Stephenson, 1979), (1/2 life ≈ 3 years) and it is highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Hexachlorobenzene or Perchlorobenzene (C_6Cl_6) is a member of a group of compounds referred to as the chlorinated benzenes.

Hexachlorobenzene (HCB) is generated as a byproduct in the productions of such compounds as perchloroethylene, carbon tetrachloride and trichloroethylene. It can also occur as a 'contaminant' in these products.

In 1945, HCB was introduced as a fungicide for cereal and seed treatment in the U.S. and although it is not a registered pesticide in Canada it is widely used in the control of wheat bunt.

HCB is very stable chemically and very resistant to biotic and abiotic degradation. It is very lipophilic and bioaccumulates rapidly. It is excreted very slowly from aquatic biota (MOE, 1984).

DDT and Related Compounds. DDT was a widely used insecticide in Ontario between 1950 and 1970. It is one of the most persistent insecticides, virtually insoluble in water, lipophilic and soluble in most organic solvents. It can bioaccumulate in fats of organisms. DDT can be metabolized to DDD and DDE. DDE is the form most commonly found in sediments and biological life. It can persist in the environment for decades. DDD (one less Cl atom than DDT) is also insecticidal. DDT undergoes significant biomagnification and is highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Methoxychlor is the methoxy analogue of DDT. It does not persist in the environment. Some organisms can metabolize methoxychlor but

those organisms that cannot may bioaccumulate small quantities of the compound. It is currently used as an insecticide in agricultural and domestic sectors in Ontario. Fish have been found to concentrate methoxychlor but the residues are lost once the source is eliminated (McEwen and Stephenson, 1979). Methoxychlor can be highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Polychlorinated Biphenyls (PCB's)

PCB's are a group of compounds consisting of a biphenyl molecule with differing numbers and arrangement of chlorine atoms. The physical and chemical properties of PCB's are determined mainly by the positions and numbers of chlorine atoms on the biphenyl molecule. As a result, individual PCB's vary in physical and chemical properties. In general, PCB's with five or more chlorine atoms are very resistant to natural degradation processes while molecules with less than five chlorine atoms can be biodegraded (Callahan et al., 1979).

PCB's are known by a variety of trade names e.g., Aroclor (USA), Phenochlor (France), Kanechlor (Japan), etc. The Aroclor series manufactured in the USA are identified by a four digit code e.g., Aroclor 1254. The first two digits (12) indicate that the preparation is a PCB mixture, while the last two digits (54) indicate the mixture has 54% chlorine.

PCB's are very inert to chemicals such as acids and alkalies, very resistant to heat and have a high dielectric constant. These properties make them ideal for uses in dielectric fluids, heat transfer agents, plasticizers, sealants and adhesives.

PCB's are virtually insoluble in water but are soluble in hydrocarbon compounds (solvents and fats). In the aquatic environment they will selectively partition to the lipid pool of organisms where they can bioaccumulate and can be transferred up the food chain. PCB's also strongly adsorb to sediments rich in organic carbon (highly organic sediments). However they have a

greater affinity for oils than for sediments (Callahan et al., 1979).

2.2.2. Assessing the Availability of PCB's and Organochlorine Pesticides from Sediment

Selective chemical extraction schemes analogous to those used in assessing the availability of metals from sediment have not been developed for PCB's and pesticides. As a result, chemical analytical techniques only provide information on the total concentrations of these compounds in sediment.

Of the total amounts of these compounds in sediment however, only a fraction may be bioavailable and release to the watercolumn may be very slow depending on the constituents of the sediment matrix. Studies have shown that pesticides such as DDT are strongly associated with the solvent extractable material (oils and greases) in sediment (Hartung and Klinger, 1970). Other studies have shown that although benthic organisms can accumulate PCB's directly from sediment, the presence of solvent extractable materials greatly inhibits this process (Meier and Rediske, 1984).

PCB's and pesticides also have strong affinities for fine particulate matter such as organic material. In the presence of organic matter, especially the refractory organics such as chitins and lignins which are very resistant to degradation, the contaminants may be rendered largely unavailable.

In general, sediments that are contaminated with PCB's and pesticides but have significant levels of organic matter and oil and grease may not present any significant short-term problems in relation to contaminant biouptake or release to the water column. There would, however, be long-term concerns related to the gradual breakdown of the oils and greases and organic matter through microbial degradation. Studies have shown that the less persistent pesticides are very readily degraded in anaerobic sediments (Muir and Yarechewski, 1984) which should result in a rapid decline in

their concentrations in anaerobic sediment once active sources have been eliminated.

With regards to the more persistent compounds such as PCB's, microbial degradation of organic matter and oils and greases in sediment may result in their gradual release to the surrounding water, in which case they would be more readily available to biota. It has been demonstrated that uptake from solution is a very rapid and effecient process compared to uptake from sediment (Fowler et al., 1978). Contaminant availability may also be increased as a result of the resuspension of contaminated sediments. Fish exposed to contaminated suspended sediments have been shown to accumulate contaminants from them (Seelye et al., 1982).

Sediment type can also influence the availability of organic contaminants. It was found that shrimp exposed to PCB contaminated mud and sand showed greater concentration factors in the sandy substrate (McLeese et al., 1980).

The availability of PCB's and pesticides from sediment would therefore be very site-specific and would be influenced by the type of sediment and the presence of oils and greases and organic matter.

2.3 BENTHIC ORGANISMS - CONTAMINANT INTERACTIONS

The most obvious adverse effects of pollutants on aquatic organisms are often the dramatic events associated with sudden mortality such as fish kills. Other effects are more subtle such as sublethal effects on reproduction, growth, etc. which may result in the diminution or elimination of sensitive organisms. Benthic organisms which inhabit aquatic bottom sediments often encounter high levels of contaminants since sediments are a repository of many contaminants introduced into the aquatic environment. Many of these organisms are restricted in their mobility and must live in and feed on the contaminated material.

In areas of high sediment contamination, some organisms cannot survive while others have a 'tolerance' for certain levels of pollution. The organisms take up contaminants from the surrounding water and through ingestion of sediments which can be altered by bacteria and digestive enzymes in the gut.

The biological focus of this investigation is on benthic macroinvertebrates that spend a considerable portion of their life cycles in bottom sediments and that are also important in the diet of fish. The oligochaetes and chironomids have been selected for the In-Place Pollutants Program because of their predominance and wide distribution in the Great Lakes (Nalepa and Thomas, 1976; Freitag et al., 1976).

The oligochaetes spend their entire life cycle in sediments and the chironomids spend the larval portion of their life cycle in bottom sediments.

Both of these groups of organisms are fed upon by certain species of fish (Sly, 1984) and in some instances may form a significant portion of the fish diet. In a study carried out in Lake Superior, it was noted that chironomid pupae constituted almost 75% of the food of young-of-the-year lake trout (Swedberg and Peck, 1984). This is especially significant in light of studies (Eadie et al., 1982; Meier and Rediske, 1984) which show that benthic organisms can take up contaminants directly from sediments and evidence (Bryan, 1979) that suggest the main source of organochlorines such as DDT and PCB's to fish is through dietary sources.

The fate of contaminants in an organism depends on a variety of physiological and biochemical factors in the organism and the chemical form of the pollutants. The levels to which organisms accumulate a certain pollutant depend on their ability to store or excrete the pollutant (Bryan, 1979). Three major types of relations between the levels of contaminants in the environment and organisms have been suggested (Bryan, 1979). These are: increases in body burden are proportional to levels being taken in from the environment; the rate of storage exceeds the rate of excretion (body burden increases with age); and levels of contaminants in the organism are independent of those in the environment (i.e. the organism excretes or metabolizes most of the contaminants encountered).

One of the major concerns with the transfer of contaminants from benthic organisms through the food chain is the progressively higher concentrations that can be retained at the higher trophic levels - a process commonly referred to as biomagnification. This has only been clearly demonstrated for the organochlorines DDT and PCB's and the metals zinc, mercury and arsenic (Biddinger and Gloss, 1984). The In-Place Pollutants Program has initiated studies that sample bottom-feeding fish (sculpins) in order to address the issue of biomagnification.

An understanding of the fate and distribution of contaminants in benthic organisms requires a good knowledge of the physical and chemical factors regulating contaminant availability in the environment, the physico-chemical factors influencing contaminant bioaccumulation in organisms, the influence of organism size, age and sex to contaminant uptake and the significance of food and water as routes of uptake and habitat. Much progress has been made to advance our knowledge in these areas (Biddinger and Gloss, 1984; Bryan, 1975). However, there are still a number of gaps to be bridged in order to obtain a comprehensive understanding of the fate and significance of various levels of environmental contaminants.

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Volume

3

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THE IN-PLACE POLLUTANTS PROGRAM

VOLUME III

PHASE 1 STUDIES

October, 1987

Ontario
Ministry of the Environment

The Honourable
Jim Bradley
Minister

Gary S. Posen
Deputy Minister

THE IN-PLACE POLLUTANTS PROGRAM

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PREFACE

The In-Place Pollutants Program addresses the impact of contaminants in sediment on overlying water quality and aquatic biota with the aim of developing strategies for the management of contaminated sediments.

This report, Volume III, describes the field and laboratory studies carried out in the Phase 1 studies and discusses the findings. Companion volumes will provide the following:

Volume I - A Program Overview (Feb. 1987)

Volume II - Background and Theoretical Concepts (Feb. 1987)

Volume IV - Phase 1 Data Summary (Oct. 1987)

Subsequent phases of the In-Place Pollutants studies will be reported in other volumes of this series.

The In-Place Pollutants Program of the Ministry of the Environment is supported in part by funds received from Environment Canada under terms of the Canada-Ontario Agreement (COA) on Great Lakes Water Quality. Activities are co-ordinated with those of the Federal government under guidance of the COA Contaminated Sediments Committee.

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SUMMARY

This report documents the studies and findings associated with the first phase of the In-Place Pollutants Program. The study addressed contaminant levels in sediments and benthic organisms from 12 locations in Lake Ontario and the Great Lakes Interconnecting Channels. The main objectives of the study were threefold:

1. To determine the spatial distribution of selected contaminants in sediment and establish the factors influencing such distribution.

2. To determine the biological and physico-chemical availability of heavy metals from sediment.

3. To determine the levels of various contaminants in benthic organisms and the relationship of these levels to those in the sediment that the organisms feed on.

The findings of the Phase 1 studies are summarized below:

SEDIMENT

General

Considerable variations in sediment type and chemistry were noted within and among the different locations sampled.

The contaminants were associated mainly with the fine-grained (silts and clays) fraction of sediment, especially the organic matter in the fine sediment fraction. The organic component (measured as loss on ignition (LOI), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), and solvent extractables (SOL)), was the major factor influencing the distribution of contaminants in sediments.

Pesticides, in general, were found at low concentrations in sediments although there appear to be constant low level discharges of these from urban storm sewers and sewage treatment plant outfalls. It appears that once the pesticides become associated with the predominantly anaerobic sediments they are readily degraded.

Lake Locations

Among the Lake Ontario locations, Windermere Basin (in Hamilton Harbour) had the most contaminated sediments followed by Toronto Harbour and Humber Bay.

High organic enrichment (LOI, TOC, SOL, TKN) was noted in Frenchman Bay and Windermere Basin. In Frenchman Bay, the enrichment appears to be due mainly to the naturally occurring peat-like substrate whereas in Windermere Basin, the enrichment appears to be due mainly to industrial material such as solvent extractables (oils and greases).

Unusually high levels of chromium were noted in Windermere Basin, Humber Bay and Toronto Harbour. This appears to be a reflection of high uses of this metal in these urban areas.

The Toronto East Headland appears to be the major source of contaminants to local sediments (around the headland), including the outer harbour.

River Locations

St. Marys River was the most contaminated of the river locations showing high levels of zinc, lead, copper, manganese, iron, chromium and solvent extractables. Most of these parameters can be attributed to discharges of metal processing (steel manufacture) wastes to the river.

The highest levels of mercury were noted in the St. Clair and Niagara Rivers.

SOMMAIRE

Le présent rapport étaie les études et les conclusions concernant la première phase du Programme d'étude des sédiments contaminés. L'étude a porté sur la teneur en contaminants des sédiments et des organismes benthiques de 12 points du lac Ontario et des voies d'eau de communication des Grands Lacs. Les objectifs principaux de l'étude couvraient trois domaines :

1. Détermination de la distribution spatiale de certains polluants dans les sédiments et recherche des facteurs influant sur cette distribution.

2. Détermination de la présence biologique et physico-chimique des métaux lourds dans les sédiments.

3. Détermination des concentrations de divers polluants dans les organismes benthiques et rapport entre ces concentrations et celles relevées dans les sédiments dont se nourrissent ces organismes.

Nous résumons ci-dessous les conclusions des études de la phase 1 :

SÉDIMENT

Généralités

On a remarqué d'importantes variations dans le type et la chimie des sédiments, dans les différents points échantillonnés et entre eux.

Les polluants se rattachaient essentiellement à la partie fine (limons et argiles) des sédiments, en particulier la matière organique dans la partie de sédiments fins. Le composant organique (déterminé d'après la perte au feu ‹PAF›, le carbone organique total ‹COT›, l'azote Kjeldahl total ‹AKT› et les composés extractibles solvants ‹CES›) a été le facteur principal agissant sur la distribution des polluants dans les sédiments.

En général, on a rencontré des pesticides en faibles concentrations dans les sédiments, mais il semble en exister un faible apport constant venant des déversements des égouts pluviaux urbains et des stations de traitement des eaux usées. Il semble que les pesticides se décomposent facilement après leur association aux sédiments à prédominance anaérobique.

Points du lac étudiés

Parmi les points du lac Ontario, le bassin de Windermere (dans le port d'Hamilton) possédait les sédiments les plus contaminés, suivi du port de Toronto et de la baie de la rivière Humber.

On a remarqué un fort enrichissement organique (PAF, COT, CES et AKT) dans la baie Frenchman et le bassin de Windermere. Dans la baie Frenchman, l'enrichissement paraît provenir essentiellement d'un substrat tourbeux naturel, alors que dans le bassin de Windermere, il proviendrait surtout de matières industrielles comme les composés extractibles solvants (huiles et graisses).

On a relevé des niveaux anormalement élevés de chrome dans le bassin de Windermere, la baie Humber et le port de Toronto, ce qui s'expliquerait par l'utilisation intense de ce métal dans ces zones urbaines.

Le promontoire de Toronto Est semble être la source essentielle de polluants dans les sédiments locaux (au voisinage du promontoire), y compris le port extérieur.

Points en rivière

La St. Marys était la plus contaminée des rivières, avec des niveaux élevés des élements suivants : zinc, plomb, cuivre, manganèse, fer, chrome et composés extractibles solvants. On peut attribuer la plupart de ces paramètres au rejet de déchets de traitement des métaux (sidérurgie) dans la rivière.

On a noté les concentrations les plus élevées de mercure dans les rivières St. Clair et Niagara.

À l'exception de la rivière St. Marys et du mercure dans les rivières St. Clair et Niagara, les sédiments des voies d'eau de communication étaient relativement propres, approximativement analogues à ceux du littoral de l'est de Toronto, qui possède les sédiments les plus propres de tous les points échantillonnés.

With the exception of St. Marys River and mercury in the St. Clair and Niagara Rivers, the sediments of the interconnecting channels were relatively clean, approximating those of the Eastern Toronto Waterfront which had the cleanest sediments among all locations sampled.

BENTHIC ORGANISMS

The benthic populations in many of the areas sampled were reduced to two species of oligochaetes (T. tubifex and Limnodrilus hoffmeisteri). These two species appear to be more tolerant of high levels of contamination such as exist in Toronto Harbour and Humber Bay.

At some stations with heavily contaminated sediments such as Windermere Basin and St. Marys River, there appeared to be a toxic influence on biota. Although the sediment provided a suitable physical substrate, it was devoid of organisms.

The sediments at two stations in the upper St. Marys River (above the industrial discharges), one station in the St. Clair River and three stations in the St. Lawrence River had an abundance of "clean-water" benthic organisms.

Two trends in contaminant uptake were noted:

(a) Pesticides, which were measured at low concentrations in sediments were elevated in benthic tissue in the vicinity of storm sewer outfalls and sewage treatment plant discharges. Based on other MOE studies, it appears that these pesticides are discharged at low concentrations from these outfalls and are taken up by the benthic organisms in the vicinity of the discharges. Once in contact with the predominantly anaerobic sediments the pesticides are degraded within a relatively short period of time.

(b) Mercury, PCBs, copper and zinc were accumulated by the benthos from sediments. The uptake of these parameters is influenced by the organic matter content of the sediment, especially the solvent extractables (oils and greases). In areas with high levels of organic matter, uptake was very low although the levels of Cu, Zn, Hg and PCB's were generally at their highest in sediment. In contrast, the highest uptake occurred in sediments with low organic matter content.

The zinc and copper levels in organisms were not related to the total levels of these metals in sediments but appeared to be related to specific geochemical fractions. For zinc the F4 phase (moderately reducible fractions associated with iron and manganese carrier particles) was the major source to biota whereas for copper, the F3 phase (organic/sulphide) had the major influence.

CONCLUSIONS

Evidence strongly suggests that contaminated sediments are sources of contaminants to benthic organisms and can exert toxic influences on benthic organisms by completely eliminating their survival or reducing the diversity to a few tolerant species. The survival of benthic organisms in polluted sediments and the concentration of certain contaminants in the tissues of these organisms raise concerns related to the potential for transfer of these contaminants to organisms higher in the food chain.

The effects of continuing discharges such as storm sewers and sewage treatment plant discharges cannot be overlooked, since they are still of major concern in areas with contaminated sediments. Any management strategy to improve sediment quality must first address the input from these sources.

Organismes benthiques

Dans la plupart des zones échantillonnées, les populations benthiques se réduisaient à deux espèces d'oligochètes (T. tubifex et Limnodrilus hoffmeisteri). Ces deux espèces semblent tolérer le mieux les concentrations élevées de pollution présentes dans le port de Toronto et la baie Humber.

En certains points ayant des sédiments fortement pollués, comme le bassin de Windermere et la rivière St. Marys, le biotope semble subir une influence néfaste. Les sédiments représentent un substrat physique suffisant, ils sont néanmoins dépourvus d'organismes.

Les sédiments en deux points en amont de la rivière St. Marys (au-dessus des rejets industriels), en un point de la rivière St. Clair et en trois points du St-Laurent présentaient une abondance d'organismes benthiques "d'eau claire".

On a remarqué deux tendances dans les relevés de polluants :

a) Les pesticides, mesurés en faibles concentrations dans les sédiments, étaient plus concentrés dans le tissu benthique au voisinage des sorties d'égouts pluviaux et des effluents d'usines de traitement des eaux usées. D'après d'autres études du ministère de l'Environnement, il semble que ces pesticides, libérés en faibles concentrations, soient absorbés par des organismes benthiques au voisinage des rejets. Au contact des sédiments essentiellement anaérobiques, les pesticides sont alors décomposés en un délai relativement court.

b) Le benthos tire le mercure, les PCB (polychlorobiphényles), le cuivre et le zinc des sédiments. L'absorption de ces paramètres dépend du contenu en matières organiques des sédiments, en particulier de leur teneur en composés extractibles solvants (huiles et graisses). Dans les régions à teneur élevée en matière organique, l'absorption était très faible, mais les concentrations de cuivre, de zinc, de mercure et de PCB étaient généralement des plus élevés dans les sédiments. Par contre, l'absorption la plus élevée se présentait dans les sédiments à faible teneur en matière organique.

Les concentrations de zinc et de cuivre dans les organismes ne se rattachaient pas au concentrations totales de ces métaux dans les sédiments, mais elles semblaient liées à des fractions géochimiques spécifiques. La phase F4 (fractions modérément réductibles associées aux particules porteuses de fer et de manganèse) était la source essentielle de zinc pour le biotope, alors que, pour le cuivre, c'était la phase F3 (organique/sulfure).

CONCLUSIONS

Les résultats de ces études font fortement croire que les sédiments contaminés sont une source de polluants pour les organismes benthiques; ils peuvent avoir des effets toxiques sur les organismes benthiques en éliminant totalement leur survie ou en réduisant leur éventail à quelques espèces tolérantes. La survie des organismes benthiques dans les sédiments pollués et la concentration de certains polluants dans les tissus de ces organismes soulèvent des inquiétudes quant au transfert possible de ces polluants aux organismes situés en aval dans la chaîne alimentaire.

Les effets de rejets continus, comme l'effluent des égouts pluviaux et des usines de traitement des eaux usées, ne peuvent être ignorés, car ils constituent la source principale d'inquiétude dans les régions à sédiments contaminés. Toute stratégie de gestion visant à améliorer la qualité des sédiments doit d'abord s'attaquer à l'apport de ces rejets.

1.0 INTRODUCTION

In 1983, the Ontario Ministry of the Environment carried out the first phase of the In-Place Pollutants Program. The studies associated with this phase of the program were designed to obtain information on the physical and chemical characteristics of surficial sediment and the levels of contaminants in representative species of benthic invertebrates in selected areas of the Great Lakes (Sub objectives 1 and 4 as outlined in Volume II of this report).

Specifically, the studies of Phase 1 were designed to address the following objectives:

1. To obtain up-to-date information on the physical and chemical characteristics of surficial sediment in selected areas of the Great Lakes. This information will be used:

   (a) to determine the variability in contaminant distribution within and among the various study locations.

   (b) to determine the influence of sediment grain size on contaminant levels.

2. To examine the partitioning of metals among various geochemical phases of the <63 µm sediment fraction which is the fraction normally ingested by benthic organisms. This information will be used:

   (a) to estimate the biological and physico-chemical availability of metals.

   (b) to determine which phase or combination of phases contributes to the levels found in indigenous benthic species.

3. To determine contaminant concentrations in selected benthic macroinvertebrates. This information will be used:

(a) to determine which contaminants bioconcentrate in organisms and the magnitude of uptake in relation to sediment levels.

The most direct influence of contaminants in sediments is expected to be exerted on the organisms that inhabit the sediment. Such influence can include the elimination of certain species as a result of the toxic effects of contaminants (to be discussed in a future report) or elevated levels of certain contaminants in the organisms that are able to survive. This latter aspect forms the major thrust of the Phase 1 studies.

In assessing the levels of contaminants in benthic organisms, consideration must be given to the spatial variability in distribution of contaminants in sediment (Volume II of this report) on both local and regional scales. This variability can be attributed to factors such as contaminant sources, sediment type and the hydrologic conditions that influence sediment movement and deposition. As a result, the number of stations within a given location and the study locations were selected to provide an adequate data base to address this issue.

Contaminant uptake by biota depends, to a large extent, on the form in which the contaminant exists in sediment. This is especially characteristic of the heavy metals, of which only a fraction of the total levels in sediment may be bioavailable.

A laboratory approach using selective chemical leaching in addition to total digestion (bulk chemistry) was used in the Phase 1 studies to determine how the metals partition among the various geochemical fractions of sediment. This procedure offers a considerable advantage over the standard bulk chemistry procedures by providing information on the source of metals (natural vs. anthropogenic), the chemical association of metals within sediment and the biological and physico-chemical (Eh/pH related) availability of metals.

This report describes the field and laboratory studies associated with the Phase 1 studies and discusses the findings. Because of the large data base and number of statistical analyses carried out, only pertinent information will be provided in this volume. Other information will be presented in Volume IV of this report series.

2.0 METHODS

2.1 Field Sampling

During the 1983 field season, 87 stations were sampled from 12 locations in Lake Ontario and four of the Great Lakes Interconnecting channels. The locations and number of stations are given in Table 2.1.

2.1.1 Sediment

Sediment collection was carried out using a 23 cm x 23 cm, Ponar grab sampler. Sample jars were filled with the top 5 cm of sediment from the ponar. pH and Eh readings were taken for each sediment sample in the field with a Corning pH and Eh meter.

The sediment samples were kept at 4°C, returned to Toronto and submitted for bulk chemical analysis on the entire sediment matrix and sequential extraction analysis on the <63 µm fraction.

2.1.2 Benthic Invertebrates

Sediment collected by the Ponar grab sampler was sieved through a U.S. #30 mesh wash bucket. The sieved samples were stored in large plastic pails and transported to the laboratory where they were sorted into various taxonomic groups. The predominant organisms obtained were from the following groups: Lumbriculidae and Tubificidae.

Approximately 5-10 gms (wet weight) of tissue were required to carry out duplicate chemical analyses.

2.2 Laboratory Procedures

2.2.1 Bulk Sediment Chemistry

Sediment samples were submitted to the MOE Rexdale laboratory for bulk chemical analyses on the entire sediment matrix. The bulk chemical

TABLE 2.1 - Study Locations and Number of Stations
(See Figure 2.1 - 2.11 for Station Locations)

Study Locations	No. of Stations
Lake Ontario -	
Windermere Basin (in Hamilton Harbour)	5
Outside Hamilton Harbour	5
Humber Bay	16
Toronto Harbour	10
Ashbridges Bay	2
East Headland	5
Toronto Eastern Waterfront (Beaches, Bluffs)	9
Frenchman Bay	5
Interconnecting Channels* -	
St. Clair River	8
St. Marys River	8
Niagara River	9
St. Lawrence River (near Wolfe Island)	5

* The Detroit River was not included in the Phase 1 studies.

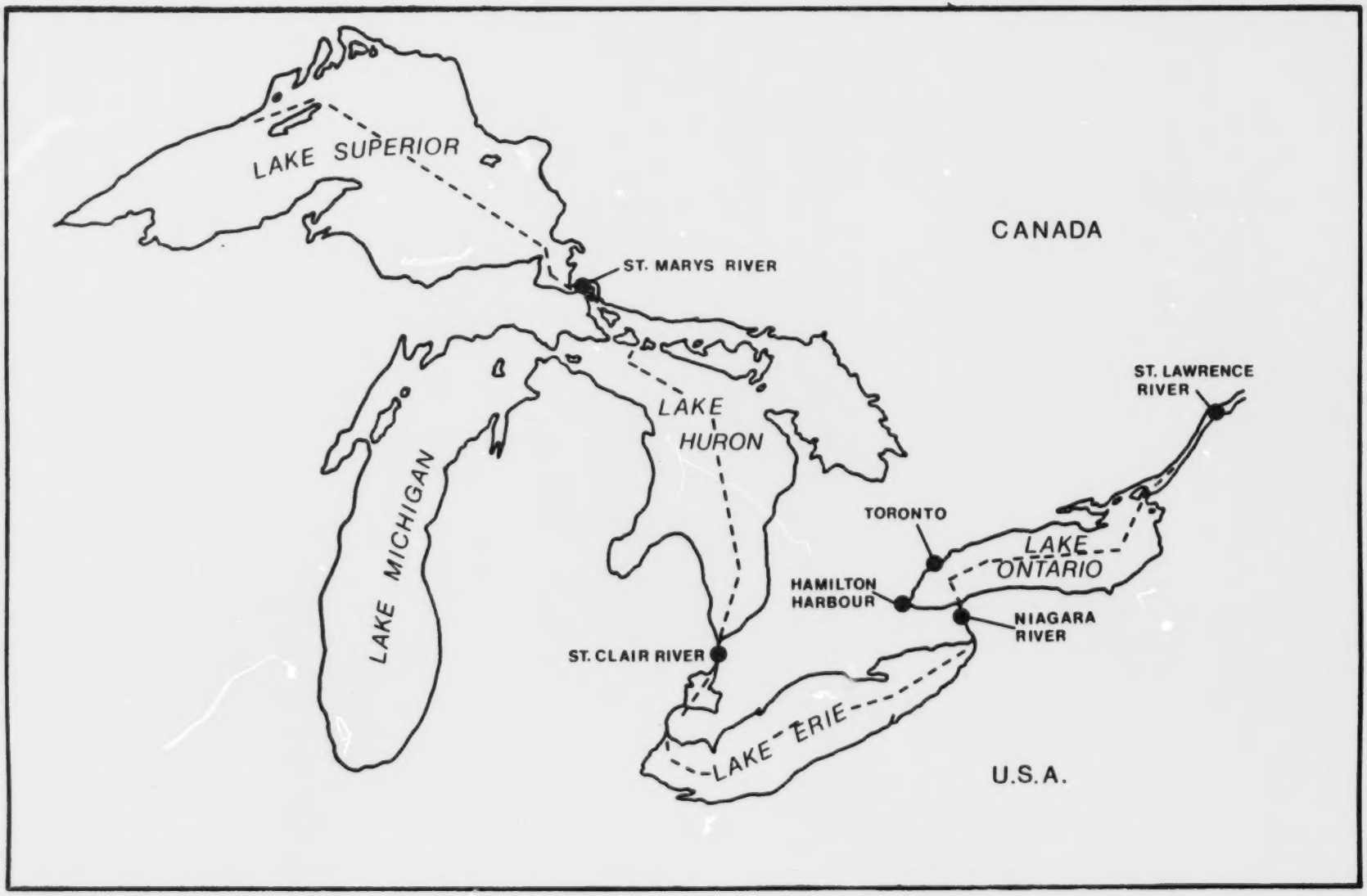


FIGURE 2.1 : PHASE 1 STUDY AREAS

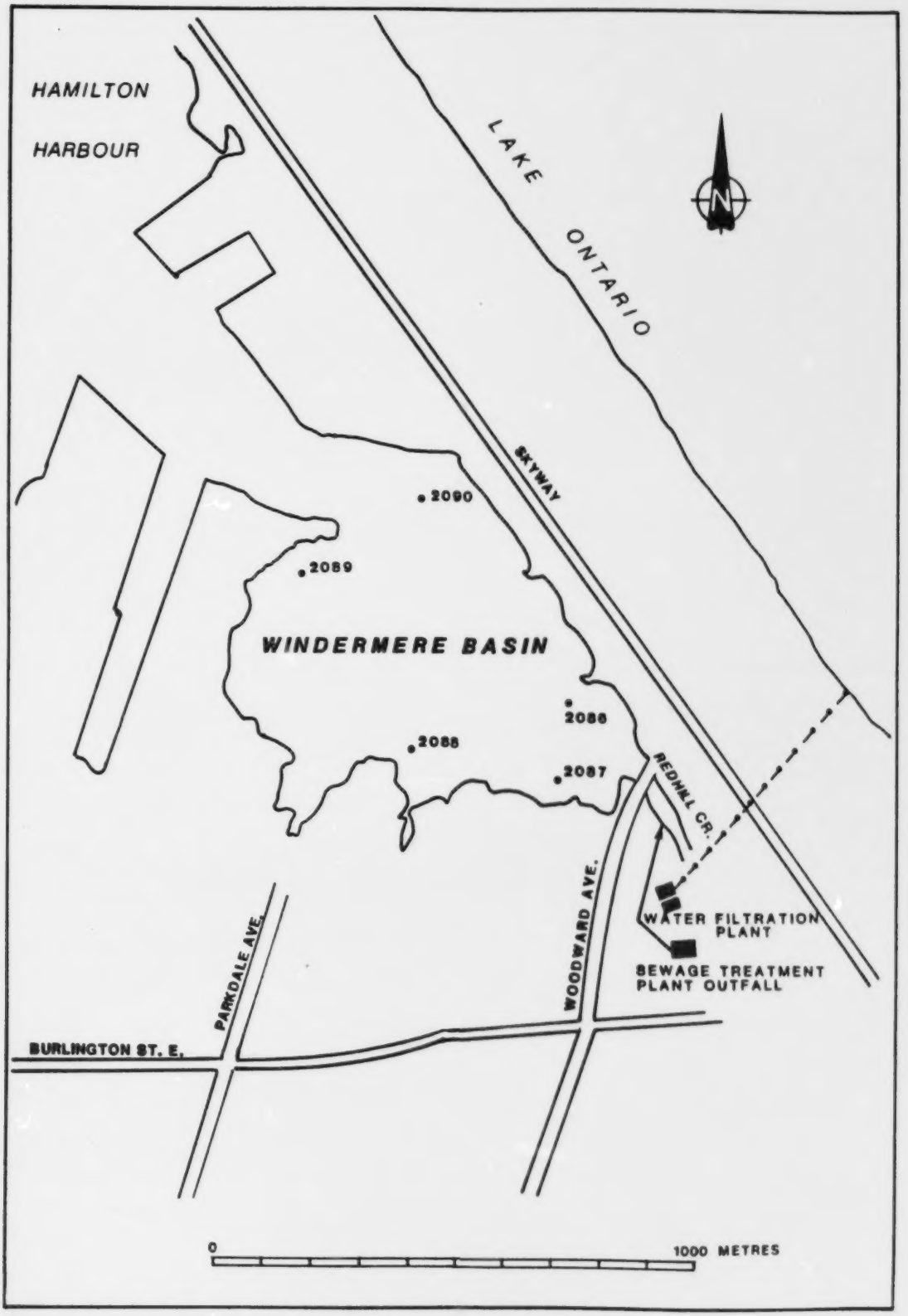


FIGURE 2.2 : STATION LOCATIONS- WINDERMERE BASIN

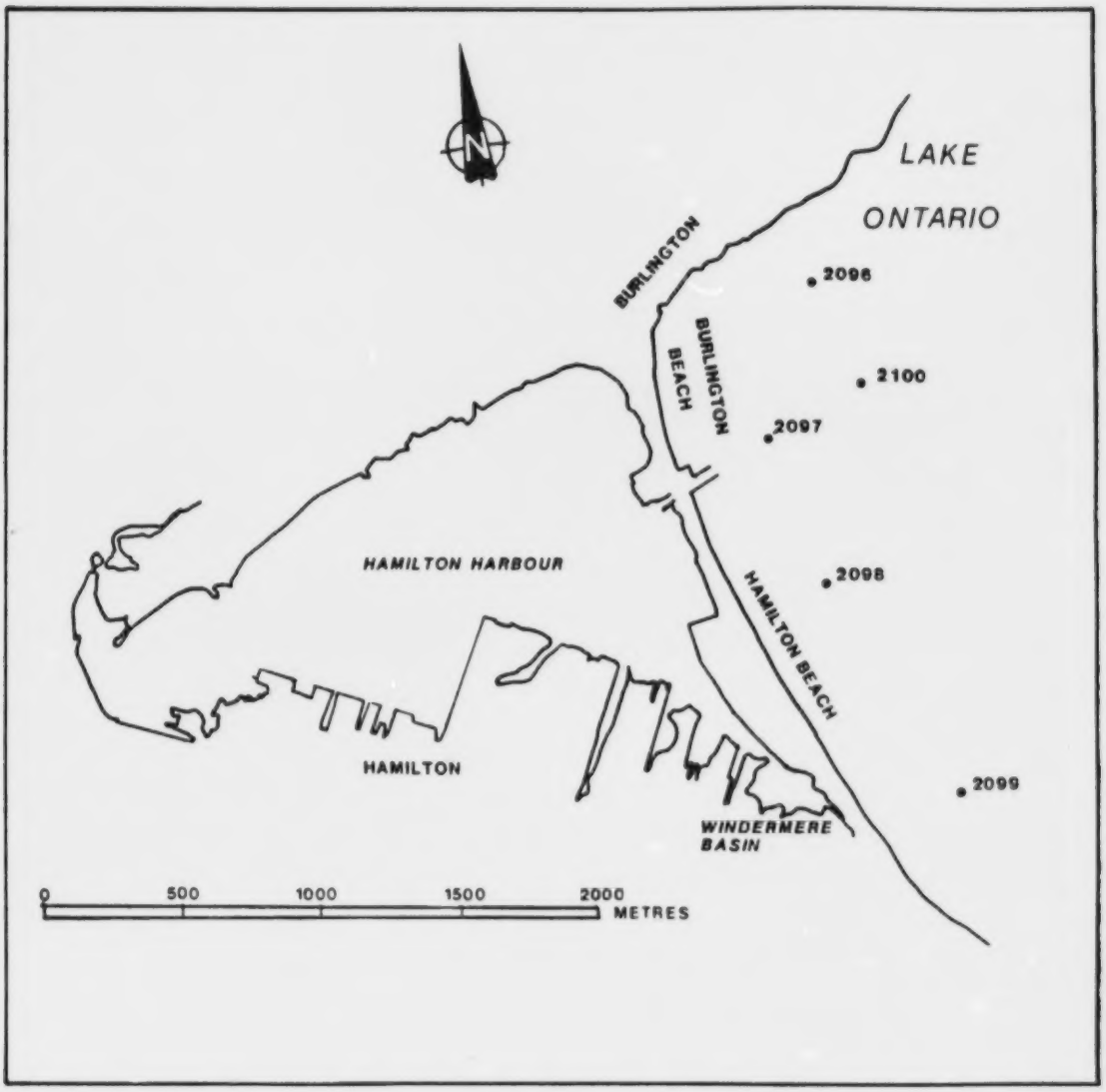


FIGURE 2.3: STATION LOCATIONS- OUTSIDE HAMILTON HARBOUR

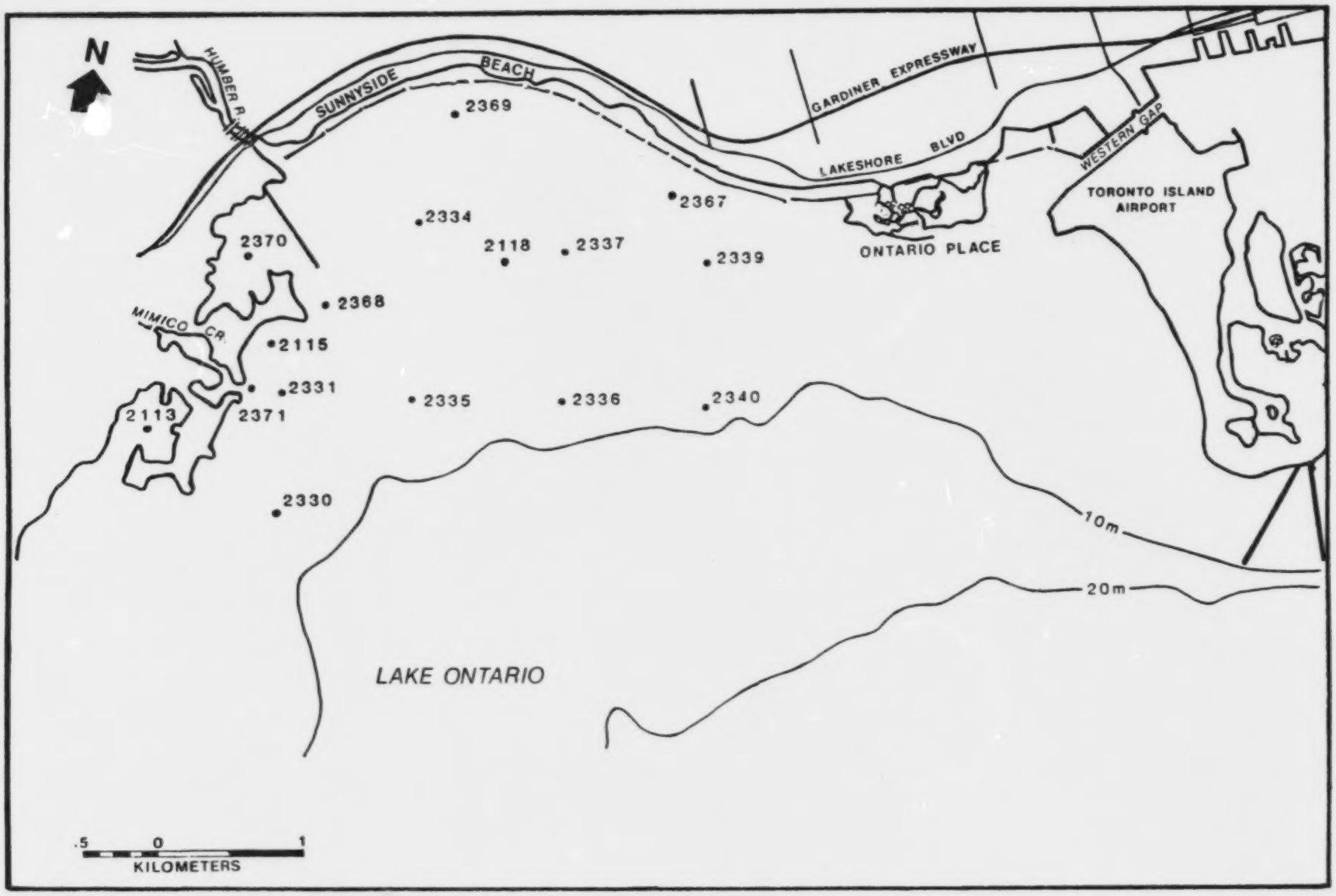


FIGURE 2.4 : STATION LOCATIONS– HUMBER BAY

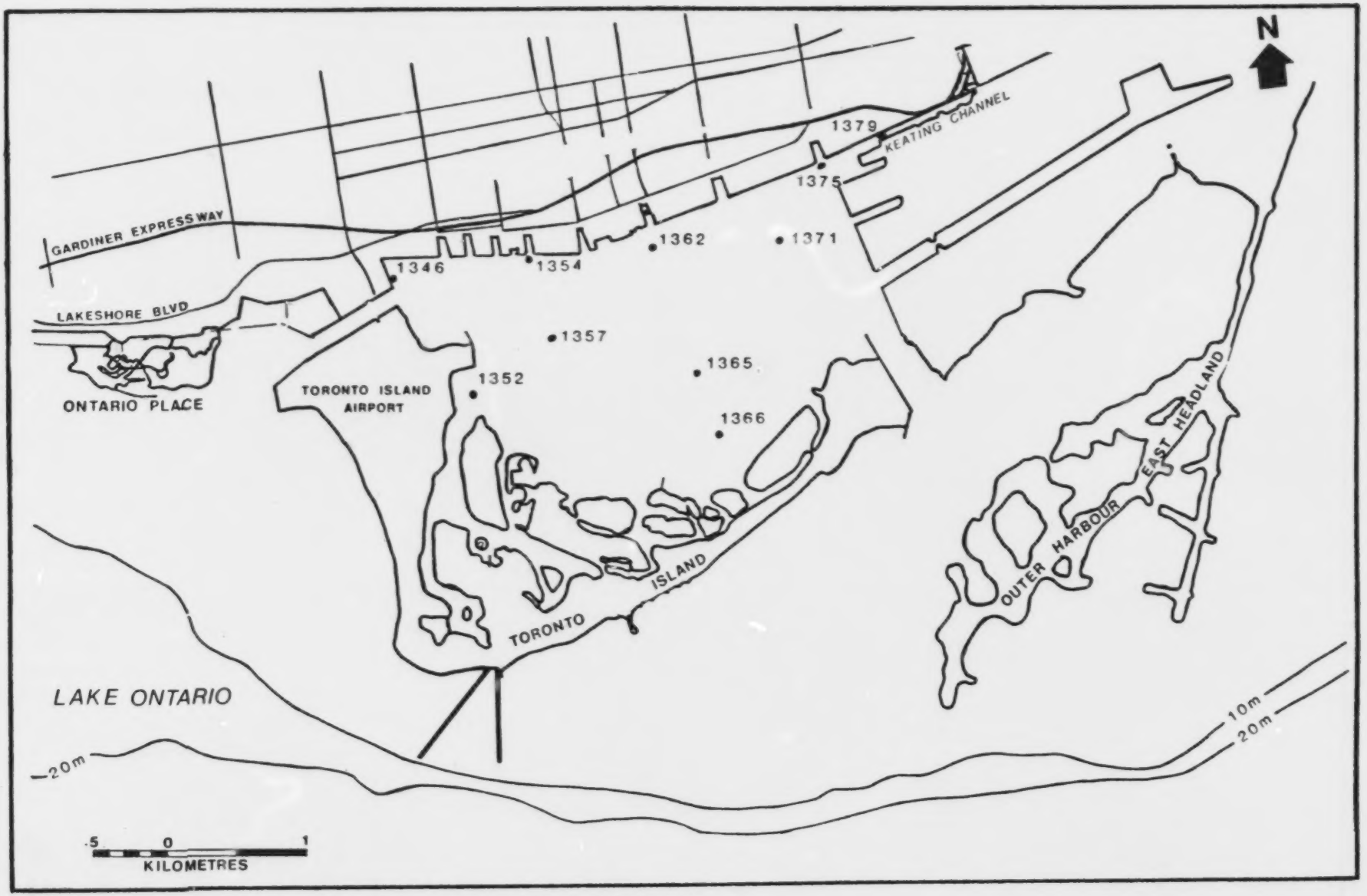


FIGURE 2.5 : STATION LOCATIONS- TORONTO HARBOUR

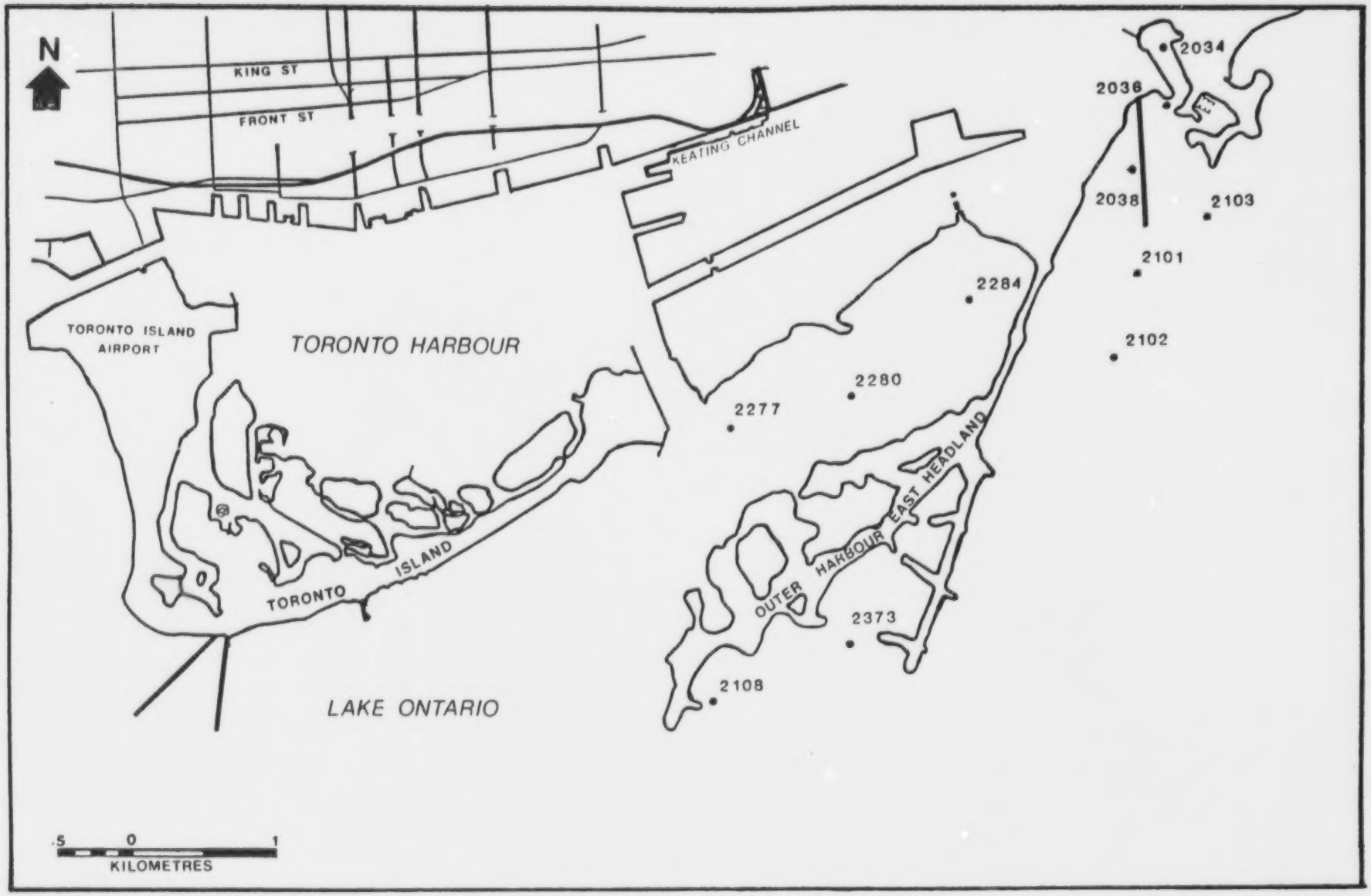


FIGURE 2.6 : STATION LOCATIONS- EASTERN HEADLAND AND ASHBRIDGES BAY

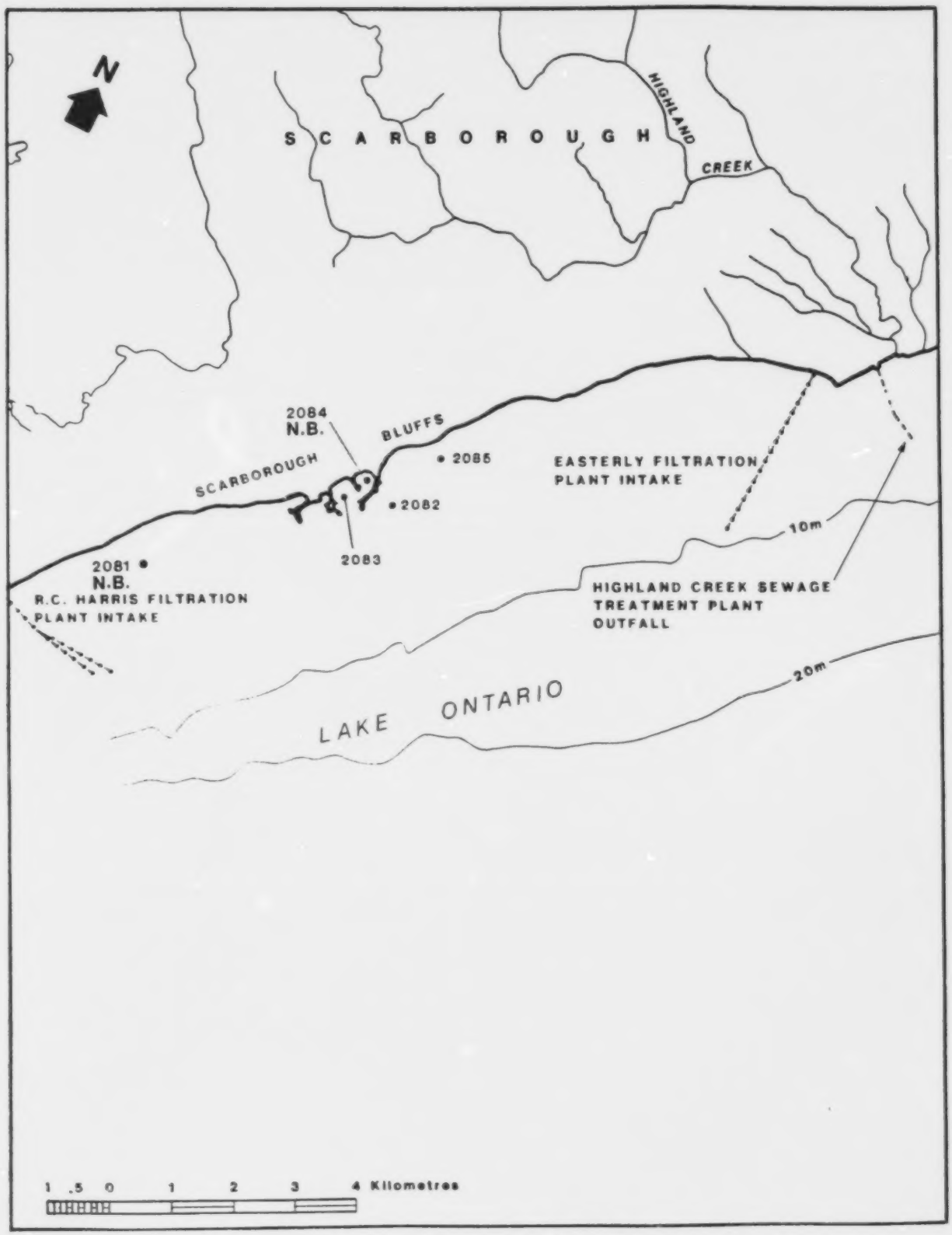


FIGURE 2.7 : STATION LOCATIONS- SCARBOROUGH BLUFFS

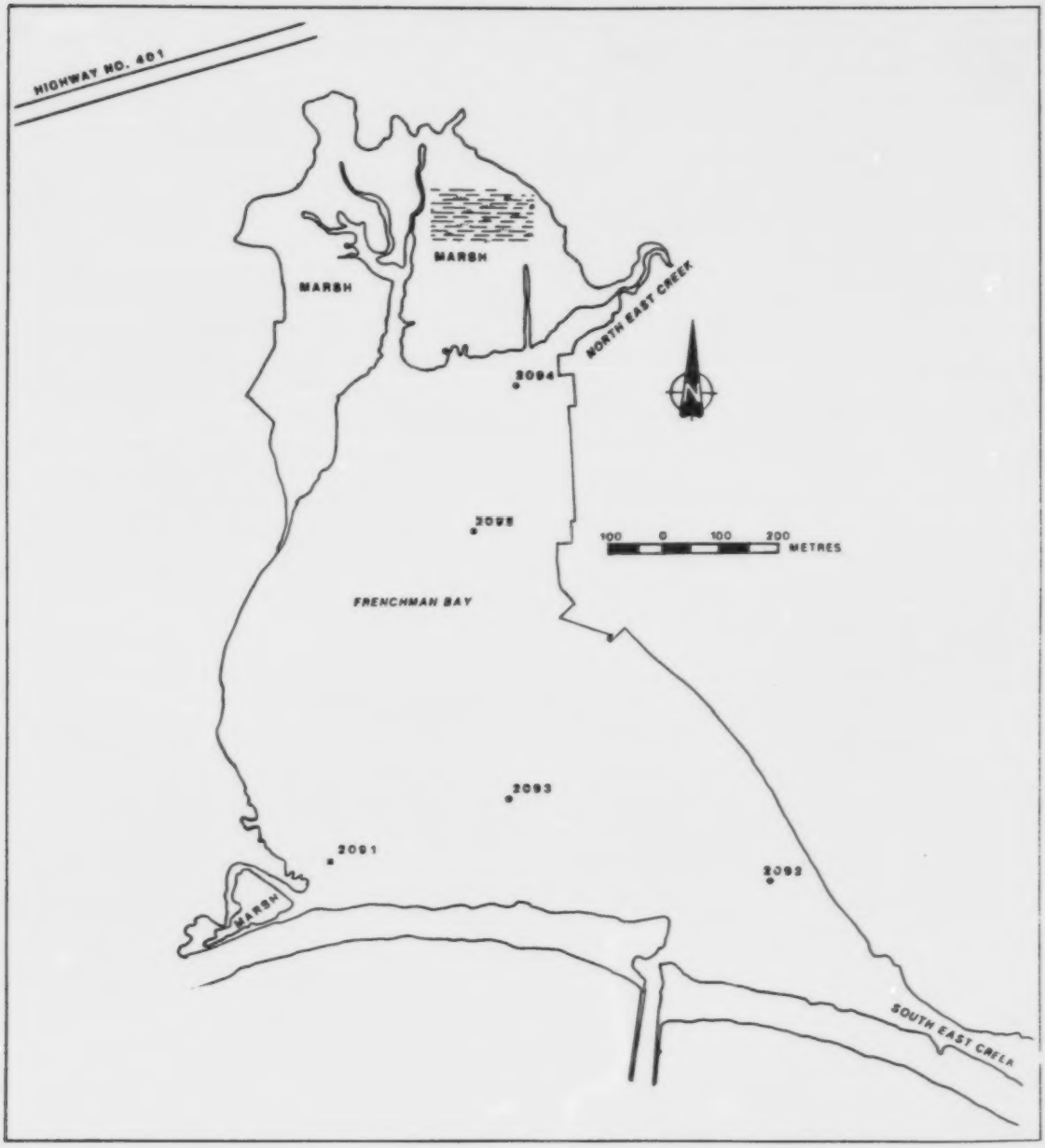


FIGURE 2.8 : STATION LOCATIONS- FRENCHMAN BAY

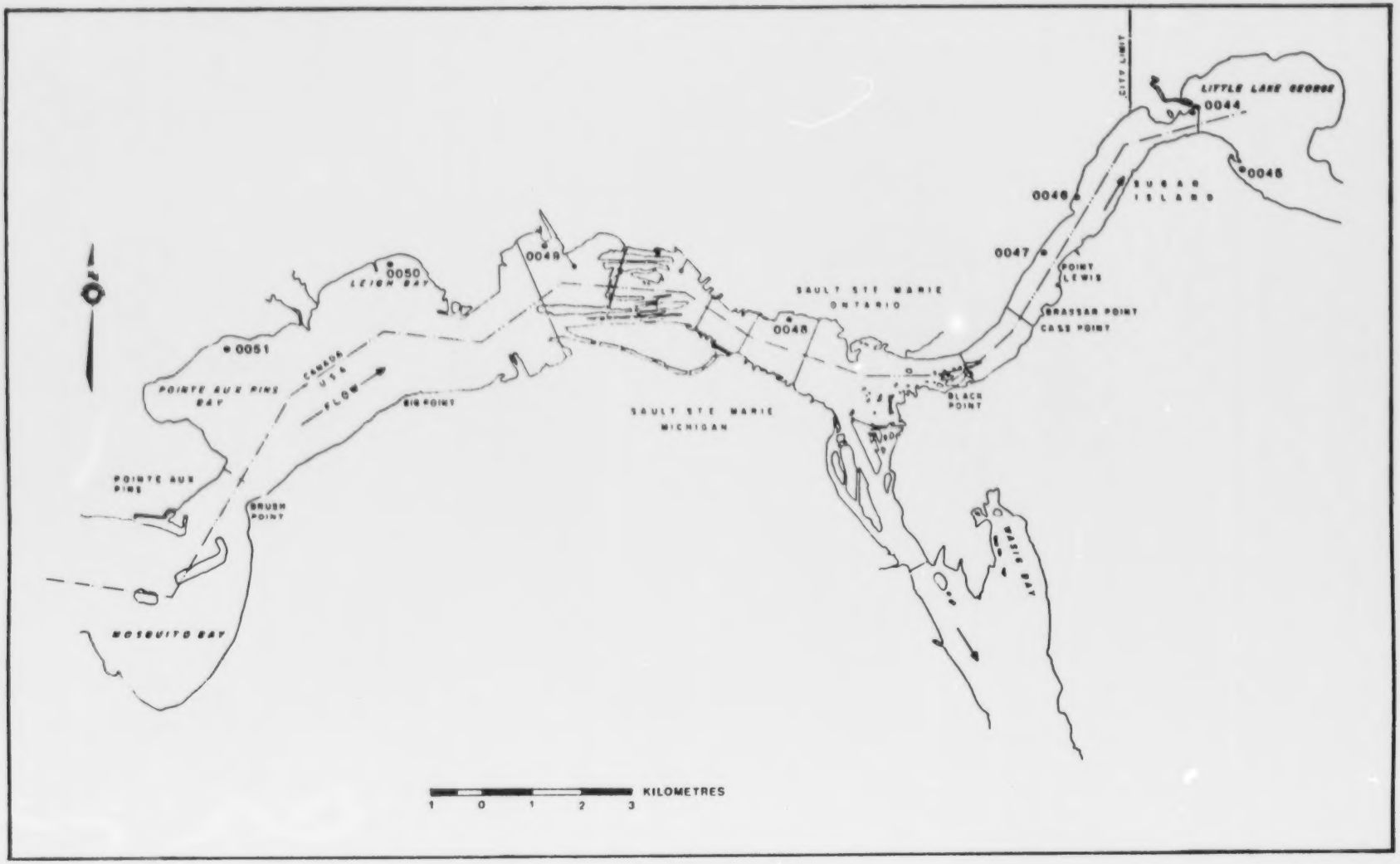


FIGURE 2.9 : STATION LOCATIONS- ST. MARYS RIVER

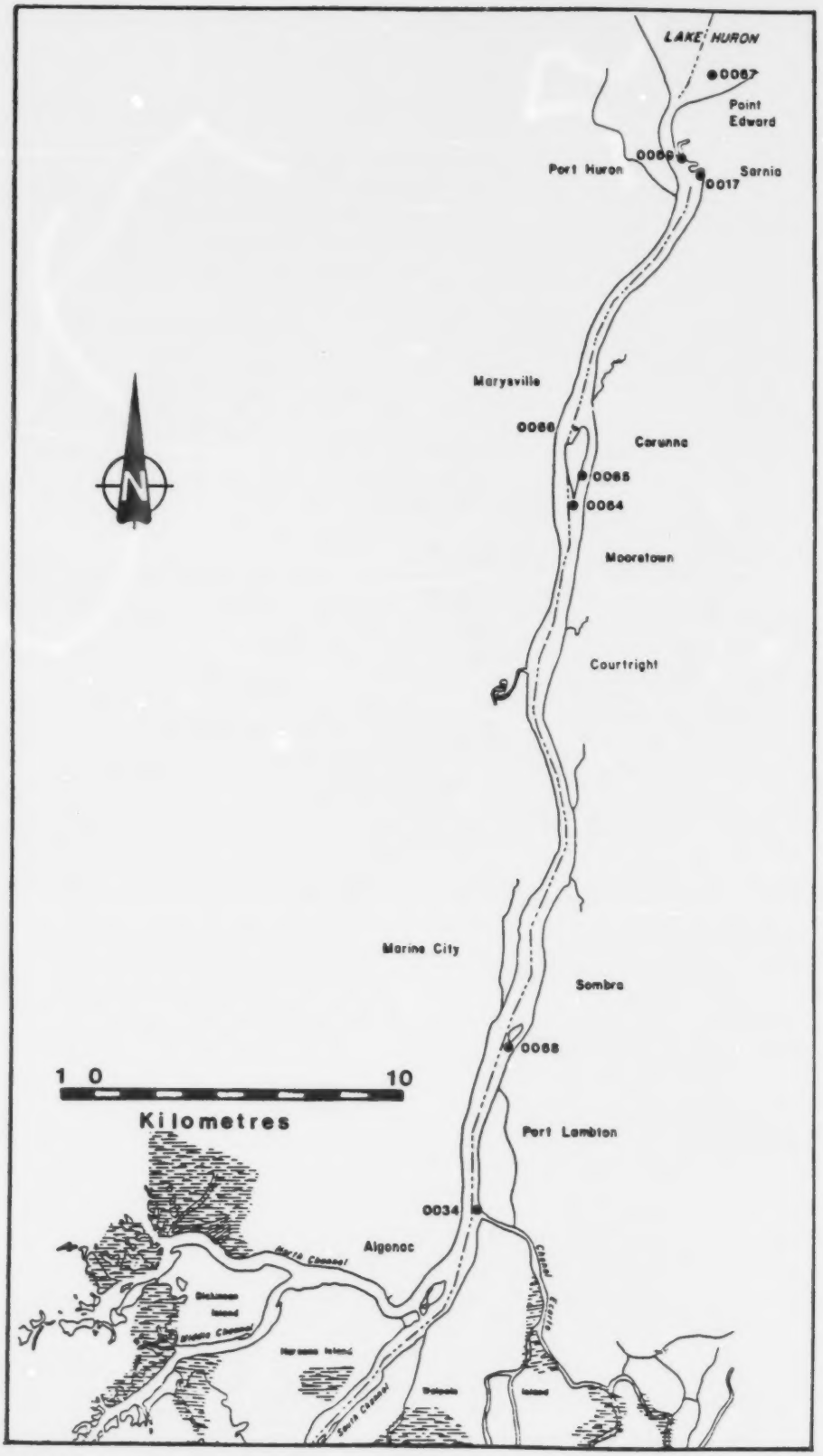


FIGURE 2.10 : STATION LOCATIONS- ST. CLAIR RIVER

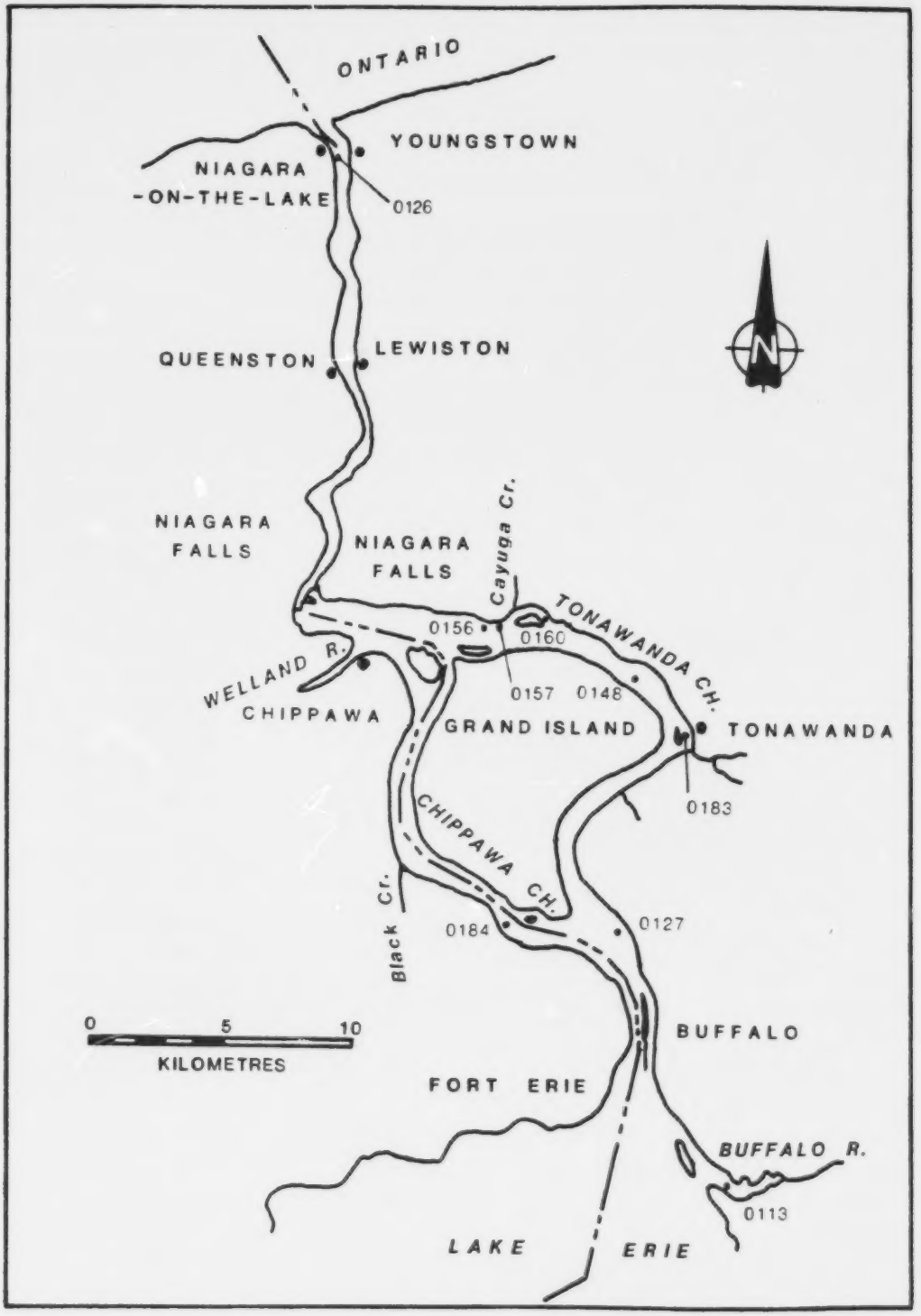


FIGURE 2.11: STATION LOCATIONS- NIAGARA RIVER

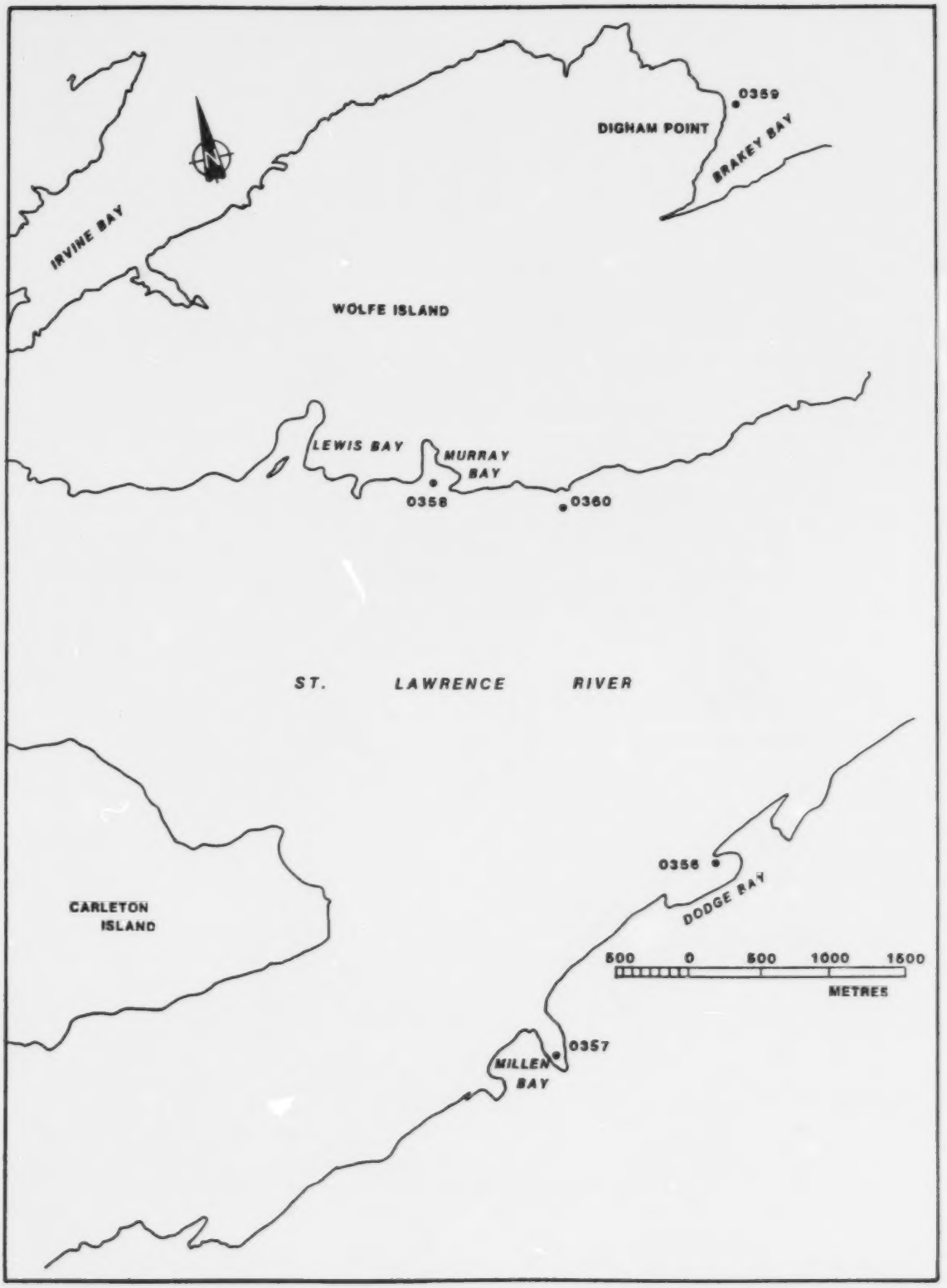


FIGURE 2.12 : STATION LOCATIONS- ST. LAWRENCE RIVER

analyses included loss on ignition, total Kjeldahl nitrogen, total organic carbon, total phosphorus, chromium, iron, manganese, mercury, cadmium, zinc, copper, lead, arsenic, solvent extractables (oil and grease), PCBs, pesticides and grain size.

Analyses were carried out in accordance with the MOE procedures (Ontario Ministry of the Environment, 1983) and all parameters were reported on a dry weight basis. Detection limits for the various analytical procedures are outlined in Volume IV of this report.

2.2.2 Metal Analysis In < 63 µm Fraction Of Sediment

Sequential Extraction

The <63 µm fraction includes sediment material such as very fine sand, silt and clay. This fraction consists of the size range of sediment that is normally ingested by benthic macroinvertebrates (Krantzberg and Bailey, 1983). This fraction was subjected to a sequential chemical leaching procedure to determine the geochemical partitioning of the metals.

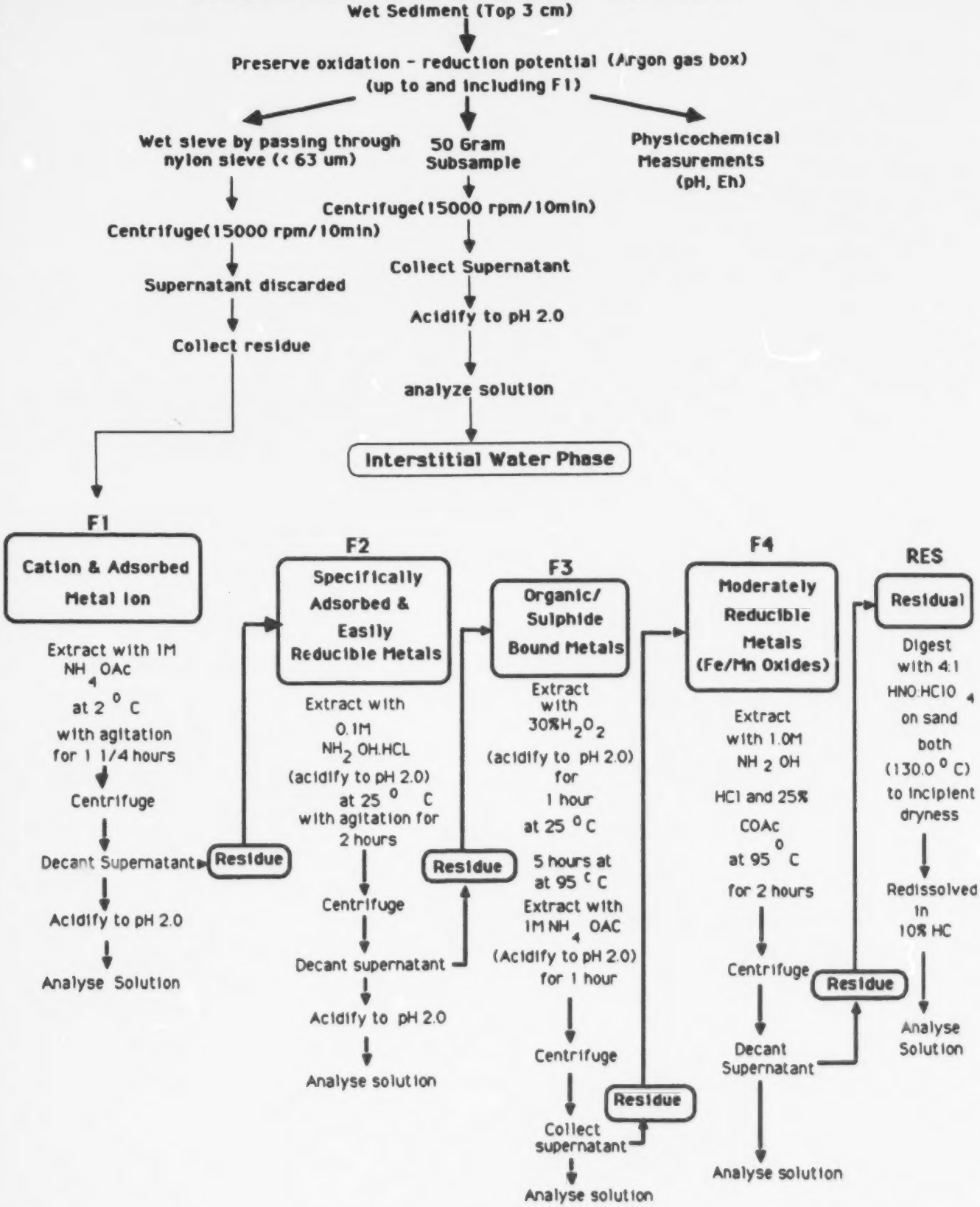
The sequential extraction procedure (see Volume II of this report and Fig. 2.13) was applied to seven metals: cadmium, copper, zinc, lead, arsenic, iron and manganese. The geochemical phases identified in the procedure were:

IW - pore water
F1 - cation exchangeable/weakly adsorbed metal ion
F2 - specifically adsorbed and easily reducible metals
F3 - organic/sulphide bound metals
F4 - moderately reducible (Fe/Mn oxides) metals
F5 - residual metal

2.2.3 Benthic Invertebrates

The benthic samples obtained in the field, were hand-picked and cleaned under running water in the laboratory. The organisms were blotted dry and then subsampled into three portions for the following:

FIGURE 2.13
SEQUENTIAL EXTRACTION OF SEDIMENT - Bound Metals


Wet Sediment (Top 3 cm)
Preserve oxidation - reduction potential (Argon gas box)
(up to and including F1)
Wet sieve by passing through nylon sieve (< 63 um)
50 Gram Subsample
Physicochemical Measurements (pH, Eh)
Centrifuge(15000 rpm/10min)
Centrifuge(15000 rpm/10min)
Collect Supernatant
Supernatant discarded
Acidify to pH 2.0
Collect residue
analyze solution
Interstitial Water Phase
F1
Cation & Adsorbed Metal Ion
Extract with 1M NH4OAc at 2 °C with agitation for 1 1/4 hours
Centrifuge
Decant Supernatant
Residue
Acidify to pH 2.0
Analyse Solution
F2
Specifically Adsorbed & Easily Reducible Metals
Extract with 0.1M NH2OH.HCL (acidify to pH 2.0) at 25 °C with agitation for 2 hours
Centrifuge
Decant supernatant
Residue
Acidify to pH 2.0
Analyse solution
F3
Organic/ Sulphide Bound Metals
Extract with 30%H2O2 (acidify to pH 2.0) for 1 hour at 25 °C
5 hours at at 95 °C
Extract with 1M NH4OAC (Acidify to pH 2.0) for 1 hour
Centrifuge
Collect supernatant
Residue
Analyse solution
F4
Moderately Reducible Metals (Fe/Mn Oxides)
Extract with 1.0M NH2OH HCl and 25% COAc at 95 °C for 2 hours
Centrifuge
Decant Supernatant
Residue
Analyse solution
RES
Residual
Digest with 4:1 HNO:HClO4 on sand both (130.0 °C) to incipient dryness
Redissolved in 10% HC
Analyse Solution

- identification	- 50 oligochaetes in 5% formaldehyde
	- 10-20 individuals of other organisms in 5% formaldehyde
- metal analysis	- the organisms were wrapped in plastic film and frozen
- PCB/pesticides scan	- the organisms were wrapped in aluminum foil and frozen.

Metal Analysis

Analyses were carried out for cadmium, copper, iron, lead, manganese, zinc, mercury and arsenic on the benthic samples . Mercury analysis consisted of digesting the organisms in a sulphuric acid - potassium permanganate solution and determinations of mercury concentrations were made by automated stannous chloride reduction and cold vapour AAS (atomic absorption spectrophotometry). The other metals were analysed by digesting the organisms in nitric acid-perchloric acid solution and chemical determinations were made by flame AAS.

PCB/Pesticide Analysis

The frozen samples were homogenized and digested for 12 hours in concentrated hydrochloric acid at 25°C. The digest was then extracted with a methylene chloride/hexane mixture. The extract was neutralized with sodium bicarbonate, dried by filtering through anhydrous sodium sulphate and evaporated.

The residue was placed in a clean-up column with 5 g of 100/200 mesh Florisil. The column was eluted successively with hexane, 25% methylene chloride/hexane and methylene chloride to obtain values for the PCBs and organochlorine pesticides. The compounds determined in each of the three fractions are shown below.

I - Hexane fraction:	PCBs, HCB, Heptachlor, Aldrin, p,p'-DDE, Mirex

II - 25% Methylene chloride/ hexane fraction:

alpha-chlordane
gamma-chlordane
o,p'-DDT, p,p'-DDD, p,p'-DDT

III- Methylene chloride fraction: Heptachlor epoxide, alpha-endosulfan, beta-endosulfan, dieldrin, endrin.

All fractions were evaporated to near dryness and made up to 1 ml in iso-octane. Each fraction was analyzed by a "Varian Vista 6000" gas chromatograph interfaced to a "Vista 402" chromatography data system.

2.2.4 Dry Weight Conversion of Contaminant Levels in Benthic Tissue

Contaminant levels in the benthic organisms were determined on a wet weight basis and the values obtained were converted to dry weight using the following relationship based on information from Howmiller (1972).

$$\begin{matrix}\text{Dry Weight} \\ \text{Contaminant} \\ \text{Value}\end{matrix} = \begin{matrix}\text{Wet weight} \\ \text{Contaminant} \\ \text{Value}\end{matrix} \times \frac{100}{15.9}$$

[where the dry weight of tissue was 15.9% of the wet weight.]

2.2.5 Correction for Gut Content

Correction for contaminants in the sediment remaining in the gut of the organism at the time of analysis was made by ashing the organisms at 500°C and determining the weight of the remaining residue.

The concentration of contaminants in the residue was calculated as follows:

$$C_{corr\ tiss} = \frac{C_{org} - (C_{sed} \times K_{ash})}{(1 - K_{ash})}$$

where C corr tiss = contaminant concentration in the benthic tissue corrected for gut content

C org = contaminant concentration (dry weight) in the organism (tissue and gut)

C sed = contaminant concentration in the < 63 µm sediment (bulk analysis of <63µm fraction)

K ash = residue remaining after ashing the organism at 500°C as a percentage of the bulk chemical value. i.e. $K\ ash = \frac{\%\ ash}{100}$

2.3 Statistical Assessment of Data

Data on metal levels in organisms and sediment are not usually normally distributed. As a result, all metal data were log-transformed to provide a normal distribution. (Shuman et al. 1977).

A statistical software package "Microstat" (developed by Ecosoft) was used to carry out the statistical analyses.

The concentrations of several variables (mainly pesticides) were generally below the analytical detection limits. In these cases, a value of 1/2 of the detection limit was substituted in the data set. Distribution characteristics of trace organics data were complicated by the presence of results less than the detection level. In these cases a value of one half the detection level was used in order to compute a reasonable estimate of the mean. Although these estimates are biased, the uncertainty associated with this procedure was assumed to be relatively negligible in comparison with the large degree of variability present in the data (i.e. standard deviations are not substantially altered by this procedure). Duplicate analyses of contaminants in benthic organisms were reported as mean values.

3.0 RESULTS

3.1 Sediment Bulk Chemistry

Results from bulk chemical analysis on the total sediment matrix are provided in Tables in Volume IV of this report and summary statistics are provided in Table 3.1. Plots showing the distribution of parameters among the stations are presented in Figure 3.1. Table 3.2 shows the study locations corresponding to the station numbers in Figure 3.1. Because pesticides were detected at very low levels in sediment and the small number of stations from which pesticide data were obtained, these compounds will not be discussed in this section but will be addressed in the section outlining the biological data.

3.1.1 General Parameter Distribution

The pH readings obtained were generally close to neutral (pH 7.0) except for two stations outside Hamilton Harbour and one station in St. Marys River, where values of less than pH 6 were detected. The reasons for these low readings were not readily apparent.

Redox potential (Eh) ranged from -520 mv to $^{+}$430 mv, with the sediment from most stations showing negative values. This indicates that most of the sediments sampled were anaerobic (i.e., reducing conditions).

Loss on ignition, which is a measure of the organic content of sediment, ranged from 0.1% to 29.0% with most stations showing values of less than 10%. The highest values noted were in Windermere Basin and Frenchman Bay.

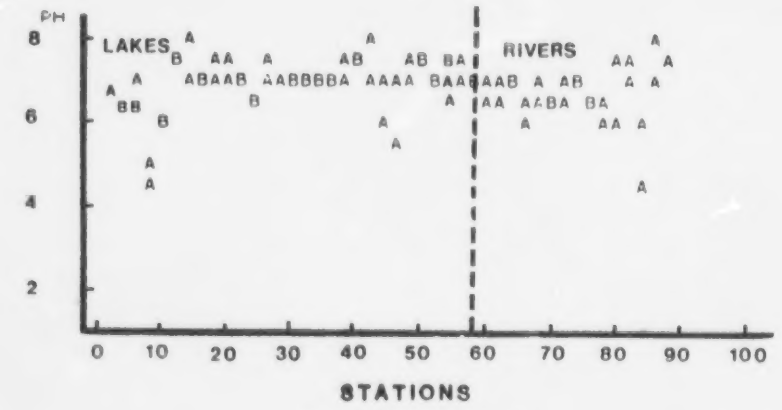
The variability in total phosphorus concentrations was much greater among the lake stations compared to the river stations. Although the range in variation among stations sampled was between 100 ppm and 9900 ppm; most of the values were below 2000 ppm. High values of total phosphorus were noted in Windermere Basin.

Table 3.1: Sediment Bulk Chemistry Summary Statistics

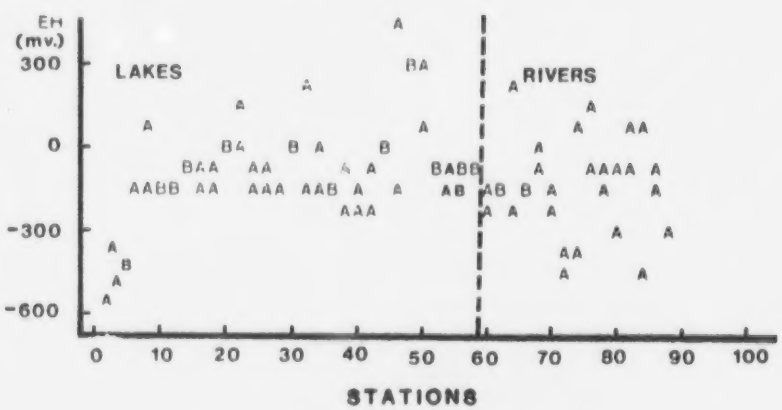
[all values in ppm(dry wt.) except pH, Eh(mv), and LOI(%)]

Parameter	N*	Mean	Std. Dev.	Median	Minimum	Maximum
Eh	87	-103	183	-155	-520	430
TP	86	1275	1648	900	100	9900
TKN	86	1862	1498	1100	100	6100
TOC	49	21395	20809	16000	10	82000
Cu	86	58.8	75.5	38	2	430
Cr	86	74.9	128	44	7.6	900
Cd	86	2.82	3.45	0.73	0.2	18
Fe	86	19204	8421	20000	4700	80000
Pb	86	108	154	56	3	570
Zn	86	218	351	110	10	2800
Mn	84	390	173	390	88	1500
SOL	84	4433	5500	2150	180	24410
PCB	81	0.19	0.3	0.03	0.02	3.1
LOI	86	5.67	4.81	4.6	0.1	29
Hg	86	0.23	0.26	0.11	0.01	2.2
As	74	5.21	3.4	4.29	0.57	16.1
pH	87	6.79	0.63	6.8	4.25	7.94

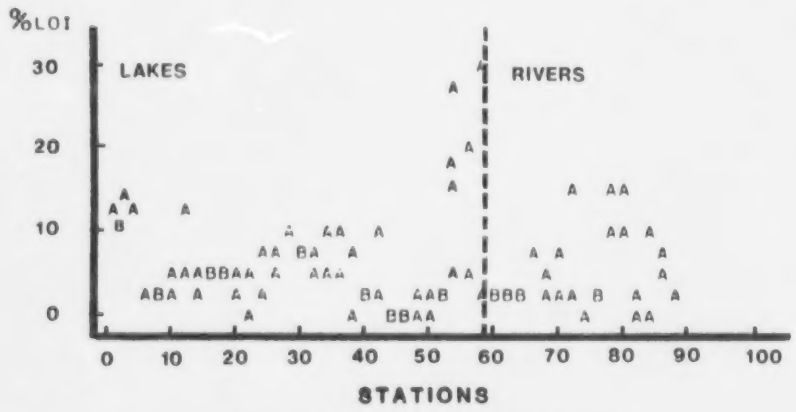
* N - Refers To The Number Of Stations



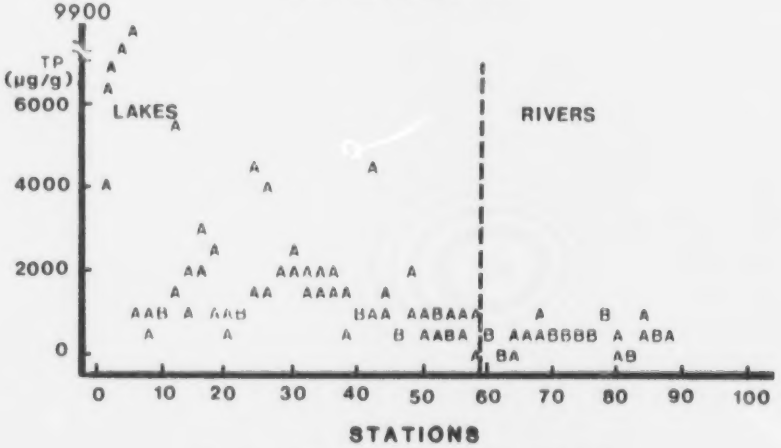
PH Distribution



Eh Distribution



Loss on Ignition Distribution

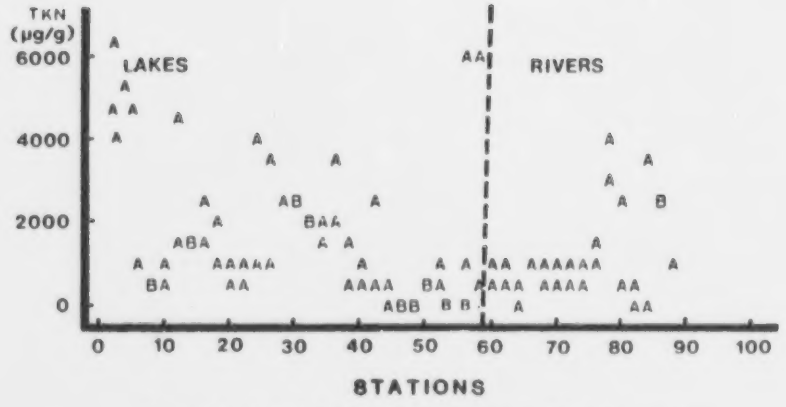


Total Phosphorus Distribution

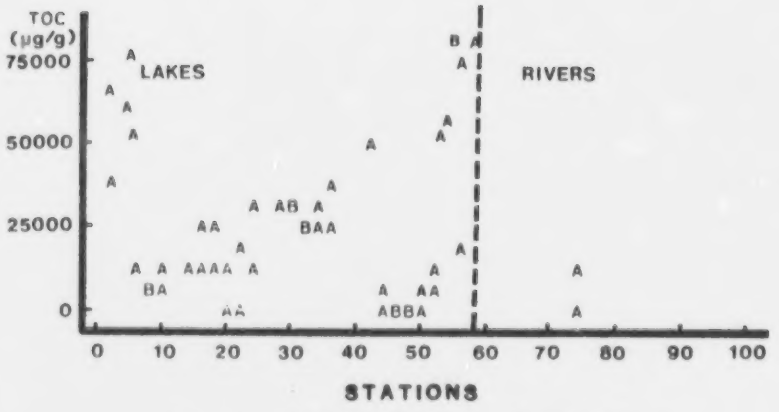
LEGEND: A = 1 OBS, B=2 OBS, ETC

For study locations corresponding to station numbers refer to Table 3.2

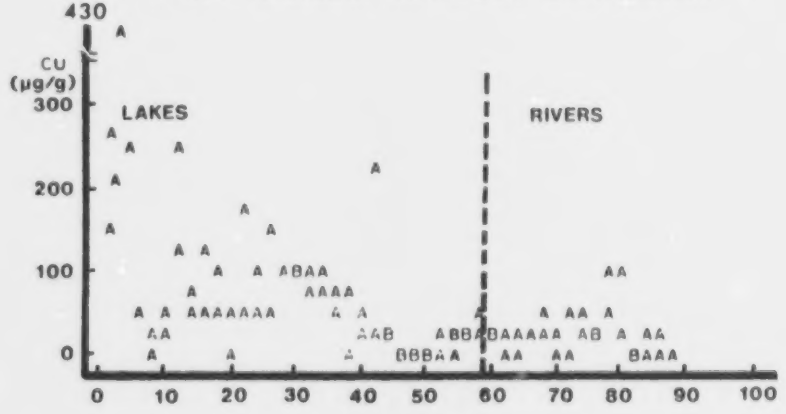
FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT



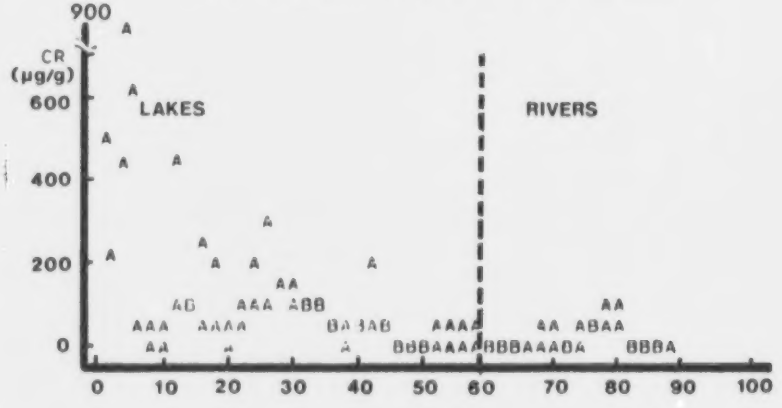
Total Kjeldahl Nitrogen Distribution



Total Organic Carbon Distribution



Copper Distribution

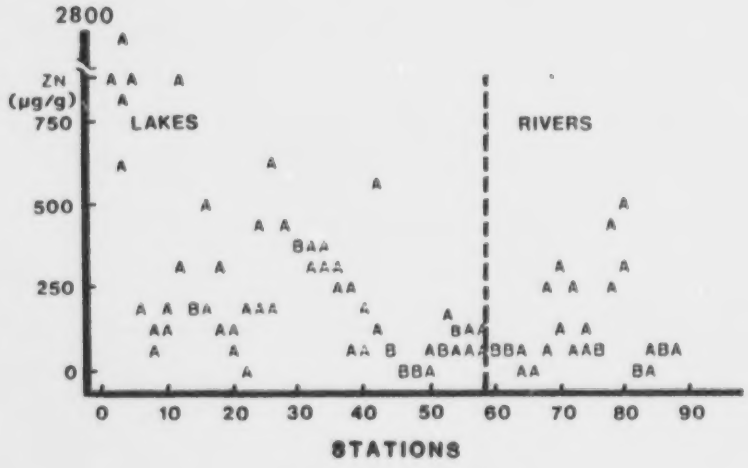


Chromium Distribution

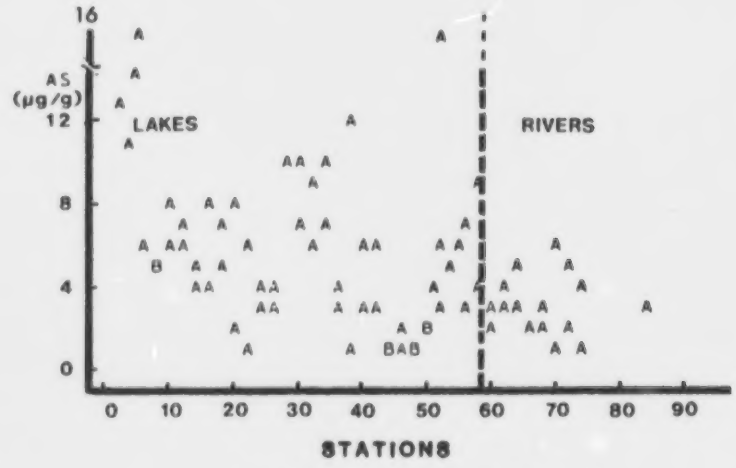
LEGEND: A=1 OBS, B=2 OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

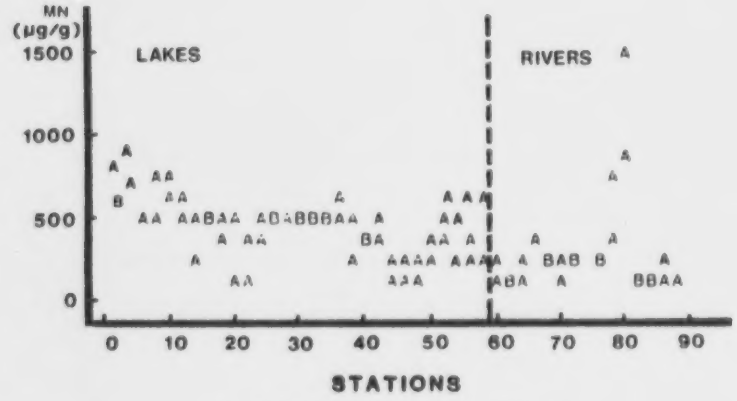
FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd



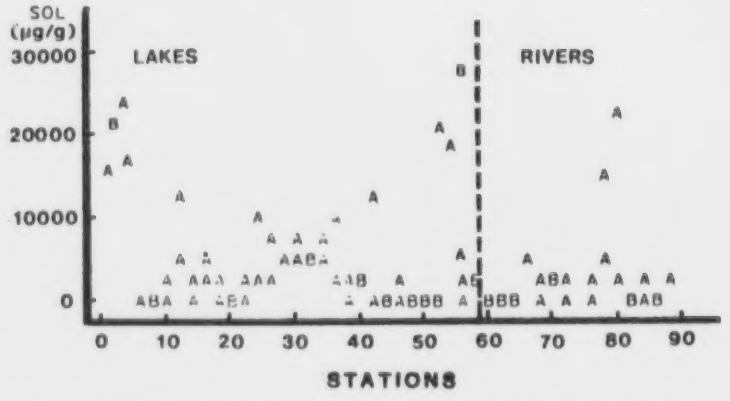
Zinc Distribution



Arsenic Distribution



Manganese Distribution

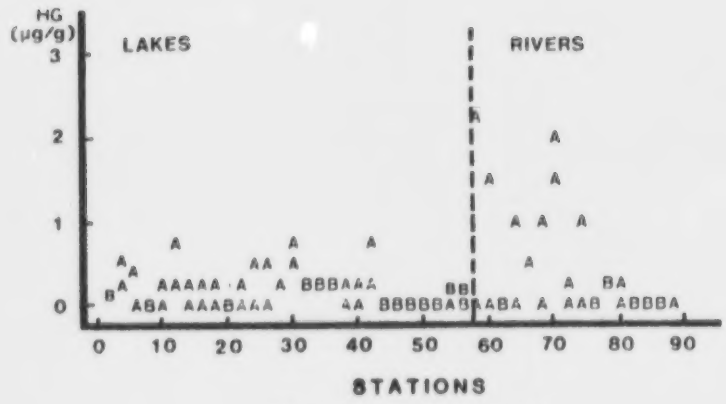


Solvent Extractables (oil and grease) Distribution

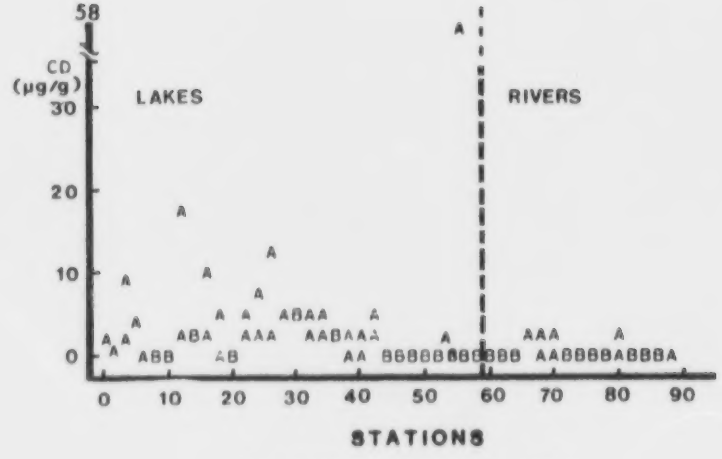
LEGEND: A=1 OBS, B=2 OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

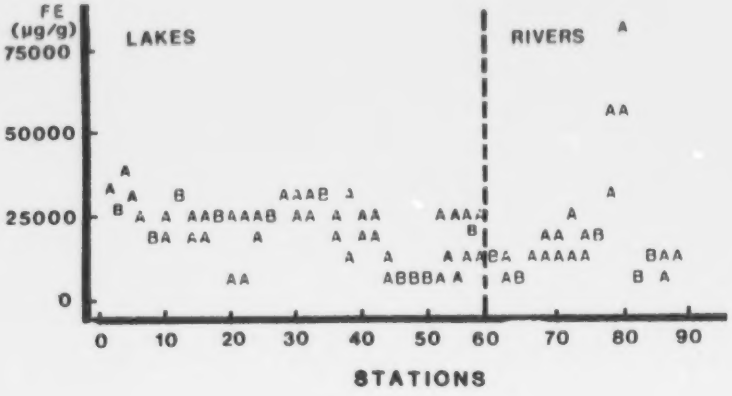
FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd



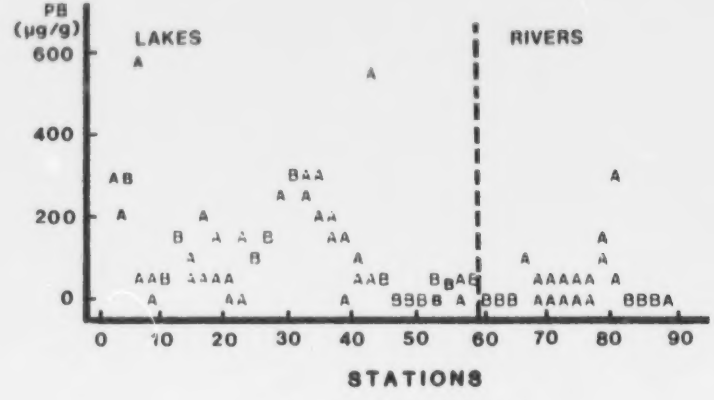
Mercury Distribution



Cadmium Distribution



Iron Distribution

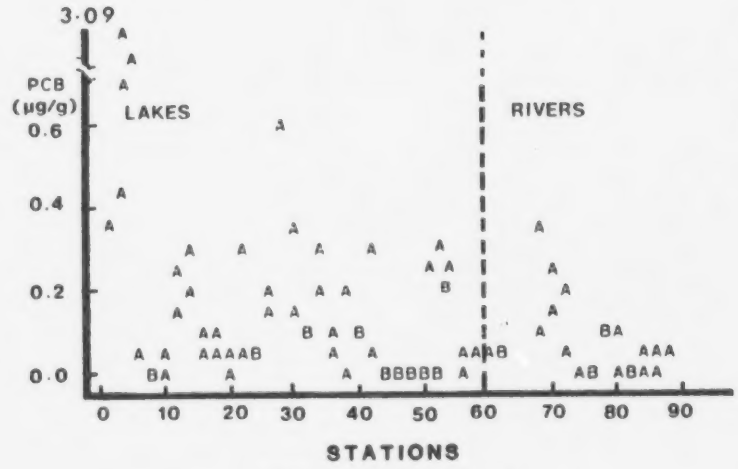


Lead Distribution

LEGEND: A=1 OBS, B=2 OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd



PCB Distribution

LEGEND: A=1 OBS, B 2=OBS, ETC.

For study locations corresponding to station numbers refer to Table 3.2

FIGURE 3.1 : DISTRIBUTION OF CHEMICAL PARAMETERS IN SEDIMENT cont'd

TABLE 3.2: STUDY LOCATIONS CORRESPONDING TO STATION NUMBERS IN FIG. 3.1

Station Numbers	Study Locations
1 - 5	Windermere Basin (in Hamilton Harbour)
6 - 10	Outside Hamilton Harbour
11 - 26	Humber Bay
27 - 36	Toronto Harbour
37 - 41	Eastern Headland
42 - 43	Ashbridges Bay
44 - 47	East side of the Headland)
	) Eastern
48 - 50	Scarborough Bluffs) Toronto
	) Waterfront
51 - 52	Bluffers Park)
53 - 57	Frenchman Bay
58 - 65	St. Clair River
66 - 74	Niagara River
75 - 82	St. Marys River
83 - 87	St. Lawrence River

Total Kjeldahl nitrogen, which like LOI, is a measure of the organic content of sediment, ranged from 100 ppm to 6100 ppm. High values were noted in Windermere Basin and Frenchman Bay.

Total organic carbon showed the widest range in concentration (10 ppm to 82,000 ppm). Most values were below 25,000 ppm with the highest levels in Windermere Basin and Frenchman Bay.

Copper, chromium and cadmium concentrations showed greater variability among the lake stations while mercury concentrations varied considerably among the river stations.

Iron, manganese and solvent extractables (oils and greases) showed considerable variations among the stations in the St. Marys River. The highest values for these parameters were noted in the St. Marys River and Windermere Basin.

Elevated levels of PCBs were found in Windermere Basin, Toronto Harbour, Humber Bay and at the Toronto East Headland in order of decreasing concentrations.

3.1.2 Contaminant Variability Among Study Locations

Based on the apparent regional differences in contaminant levels in sediment (Figure 3.1), a comparative evaluation of mean concentrations of chemical parameters obtained from the bulk chemistry analyses was carried out. The values for the various parameters are provided in Tables 3.3 and 3.4 for the Lake Ontario and the interconnecting channel locations respectively.

Among the lake stations, Windermere Basin sediment showed excessively high values for all parameters measured (except mercury which was higher in Toronto Harbour), followed by Toronto Harbour and Humber Bay. The levels of contaminants in Windermere Basin, Toronto Harbour and Humber Bay greatly exceeded the mean contaminant concentrations of Lake Ontario sediments for most parameters. Mean contaminant concentrations of Lake

Table 3.3 Mean Concentrations of Chemical Parameters In Sediment from Lake Ontario Locations

[all values in ppm dry wt. except LOI(%)]

Parameter	Windermere Basin (Hamilton Harbour)	Outside Hamilton Harbour	Humber Bay	Toronto Harbour	Toronto East Headland	Eastern Toronto Waterfront	Frenchman Bay	Lake Ontario Surficial Sediment **
Pb	348	38	104	271	83	17	54	107
Zn	1470	127	280	339	129	35	105	214
Cu	266	28	90	90	38	9	31	50
Fe	33800	20600	22169	26700	21520	13150	19200	55700
Mn	728	650	417	493	358	296	500	3200
Cr	538	31	133	92	46	19	32	48
TKN	5000	680	1780	2100	900	400	4520	ND
TP	6960	820	2100	1810	900	1040	880	2200
TOC	58000	8100	15100	29200	ND	4920	56000	ND
Sol. Ext.	20492	846	3605	5689	1926	602	1968	ND
Hg	0.35	0.07	0.22	0.47	0.17	0.02	0.05	0.65
Cd	5.24	0.46	5.00	3.93	1.54	0.36	12.27	2.50
As	13.60	5.90	4.70	6.90	5.00	0.40	8.60	3.30
LOI	14.40	2.78	4.98	7.26	3.22	1.59	17.54	1.96
PCBS	1.15	0.03	0.13	0.32	0.13	0.02	0.03	0.06

** = Whole lake mean values from R.L. Thomas and A. Mudroch (1979).

ND = No Data

Table 3.4 Mean Concentrations of Chemical Parameters in Sediment from the Great Lakes Interconnecting Channels Locations

[all values in ppm dry wt.]

Parameter	St. Lawrence River *	St. Clair River*	Niagara River *	St. Marys River *	Detroit River **
Pb	12.00	29.00	31.00	79.00	39.00
Hg	0.05	0.75	0.72	0.19	0.19
Zn	41.00	43.00	156.00	212.00	97.00
Cd	0.21	0.53	0.87	0.81	ND
Cu	12.00	15.00	29.00	37.00	22.00
Fe	11300.00	9237.00	14900.00	35087.00	14326.00
Mn	150.00	217.00	235.00	513.00	ND
Cr	17.00	13.00	24.00	40.00	24.00
TKN	1920.00	580.00	740.00	1630.00	ND
TP	640.00	250.00	640.00	530.00	ND
PCBS	0.03	0.03	0.14	0.04	0.07
Sol. Ext.	1414.00	1546.00	2000.00	6146.00	ND

* Data from Current Study (1983)

** Data from MOE 1980 Study(pers. comm. P. Kauss)

ND = No Data

Ontario sediments were obtained from Thomas and Mudroch (1979) (Table 3.3). The values represent mean concentrations for the whole lake surficial sediments (ie. depositional and nondepositional areas in Lake Ontario).

Notable exceptions were mercury, iron and manganese in Windermere Basin, Toronto Harbour and Humber Bay, total phosphorus in Toronto Harbour and Humber Bay and lead in Humber Bay.

The sediment from Frenchman Bay and Windermere Basin showed high organic enrichment based on values for LOI, TKN and TOC. For Frenchman Bay this enrichment is most likely a reflection of the peat-like substrate observed in the Bay during sampling. The relatively low levels of the other parameters in proportion to the organic content suggest that the organic enrichment of the bay is not significantly influenced by industrial/municipal discharges. An extremely high value for cadmium was obtained at one station, however this value cannot be confirmed without additional sampling. The high organic enrichment in Windermere Basin appears to be due mainly to the high levels of solvent extractables.

The sediments of Eastern Toronto Waterfront were relatively clean. This area is influenced by waves and currents which effectively minimize the deposition of fine-grained material such as silts and clays, with which any contaminant build-up would be associated.

The levels of contaminants in sediment from stations around the Toronto East Headland were considerably higher than the levels in Eastern Toronto Waterfront stations and also showed levels above those in the stations outside Hamilton Harbour (except Mn and As). The elevated levels of parameters around the East Headland relative to the Eastern Toronto Waterfront may be due to the localized deposition of material arising from the lake-filling activity at the headland.

Higher levels of mercury were noted in the St. Clair and Niagara Rivers compared to the other two interconnecting channels studied. As shown in Table 3.4, the St. Marys River had high levels of Pb, Zn, Cu, Mn, Fe, Cr

and solvent extractables compared to the other interconnecting channels. PCBs were also elevated in the Niagara River relative to other rivers (Table 3.4).

With the exception of metals and solvent extractables in the St. Marys River and mercury in the St. Clair and Niagara Rivers, the sediments of the interconnecting channels were of better quality compared to the lake stations, approximating those of the Eastern Toronto Waterfront.

In order to determine whether the differences in parameter concentrations between the rivers and lake stations were statistically significant, a normal test statistic (Z) was used to compare the means. The results are summarized in Table 3.5. There were no significant differences in the mean concentrations of Zn, Hg, Fe, TKN, Solvent extractables and PCBs between the lake and river stations. However, TP, Cu, Cr, Cd, Pb, Zn and As were significantly different, with much higher levels in the lake stations.

3.1.3 Inter-relationships Among Sediment Parameters

Parameters with similar distribution patterns in sediment usually show strong association when correlation coefficients between pairs of parameters are calculated. Very high positive correlations between parameters usually result when contaminants discharged from the same source are associated with the same "carrier particles" that behave similarly in the aquatic environment.

Correlation coefficients between various pairs of sediment parameters (chemical and grain size) are shown in Tables 3.6 and 3.7 for the lake and river stations respectively. The significance of the various relationships among the chemical parameters are summarized in Table 3.8.

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*"Carrier Particles" - refers to particulate matter to which contaminants are adsorbed. [The important *"carrier particles" with which contaminants are associated include organic material (measured as LOI, TOC or TKN), the hydrous oxides of Fe and Mn (mainly for metals) and clay minerals.]

TABLE 3.5: SUMMARY OF LAKE - RIVER COMPARISON

PARAMETER	Z	SIG-LEVEL	COMMENT
TP	6.40	≤.01	Significant
TKN	1.40	.16	Not Significant
CU	4.09	≤.01	Significant
CR	4.35	≤.01	Significant
HG	-1.73	.08	Not Significant
CD	4.66	≤.01	Significant
FE	0.49	.62	Not Significant
PB	3.79	≤.01	Significant
ZN	2.45	≤.01	Significant
AS	3.47	≤.01	Significant
MN	1.94	.05	Significant
SOL	0.10	.92	Not Significant
PCB	1.53	.13	Not significant

(Significant at $\alpha \leq .05$)

Table 3.6 Correlation Coefficients (r) for Parameters in Sediment - Lake Stations

	% LOI	TP	TKN	TOC	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	SILT	CLAY	SAND	CSIL	FSAND	Cd
% LOI	1.00																		
TP	0.54	1.00																	
TKN	0.93	0.63	1.00																
TOC	0.84	0.47	0.89	1.00															
Cu	0.66	0.70	0.75	0.79	1.00														
Cr	0.64	0.90	0.72	0.66	0.90	1.00													
Hg	0.65	0.70	0.70	0.71	0.82	0.80	1.00												
Fe	0.81	0.66	0.78	0.72	0.67	0.72	0.71	1.00											
Pb	0.73	0.68	0.77	0.82	0.87	0.84	0.90	0.77	1.00										
Zn	0.75	0.82	0.80	0.77	0.88	0.93	0.86	0.83	0.93	1.00									
Mn	0.73	0.50	0.72	0.65	0.55	0.55	0.52	0.90	0.60	0.70	1.00								
SOL	0.72	0.80	0.81	0.76	0.84	0.86	0.87	0.68	0.88	0.90	0.54	1.00							
PCB	0.56	0.73	0.60	0.57	0.77	0.79	0.83	0.59	0.79	0.82	0.39	0.81	1.00						
SILT	0.77	0.44	0.82	0.83	0.73	0.61	0.69	0.80	0.75	0.74	0.74	0.64	0.53	1.00					
CLAY	0.72	0.40	0.75	0.78	0.69	0.59	0.64	0.77	0.79	0.70	0.61	0.62	0.49	0.82	1.00				
SAND	-0.52	-0.52	-0.54	-0.46	-0.54	-0.61	-0.47	-0.51	-0.51	-0.57	-0.45	-0.58	-0.51	-0.40	-0.37	1.00			
CSIL	0.37	0.24	0.33	0.36	0.23	0.20	0.18	0.45	0.13	0.24	0.53	0.13	0.12	0.40	0.11	0.03	1.00		
FSAND	-0.46	-0.40	-0.50	-0.45	-0.52	-0.51	-0.54	-0.59	-0.52	-0.54	-0.55	-0.50	-0.30	-0.54	-0.46	0.49	-0.24	1.00	
Cd	0.64	0.62	0.73	0.67	0.81	0.75	0.71	0.56	0.72	0.71	0.42	0.73	0.68	0.59	0.59	-0.45	0.21	-0.44	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.30

N = 44

Table 3.7 Correlation Coefficients (r) for Parameters in Sediment - River Stations

	% LOI	TP	TKN	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	SILT	CLAY	SAND	CSIL	FSAND	Cd
% LOI	1.00																	
TP	0.24	1.00																
TKN	0.79	0.46	1.00															
Cu	0.88	0.41	0.75	1.00														
Cr	0.77	0.46	0.66	0.83	1.00													
Hg	0.52	0.57	0.36	0.66	0.54	1.00												
Fe	0.63	0.30	0.40	0.65	0.90	0.39	1.00											
Pb	0.85	0.47	0.65	0.90	0.93	0.71	0.82	1.00										
Zn	0.81	0.41	0.50	0.88	0.86	0.80	0.78	0.95	1.00									
Mn	0.70	0.16	0.43	0.69	0.88	0.35	0.95	0.81	0.78	1.00								
SOL	0.74	0.50	0.61	0.85	0.82	0.71	0.75	0.89	0.87	0.73	1.00							
PCB	0.50	0.49	0.31	0.71	0.49	0.78	0.32	0.63	0.74	0.37	0.58	1.00						
SILT	0.71	0.28	0.92	0.74	0.59	0.31	0.28	0.57	0.44	0.34	0.57	0.27	1.00					
CLAY	0.77	0.01	0.60	0.65	0.49	0.28	0.41	0.51	0.50	0.55	0.53	0.36	0.59	1.00				
SAND	-0.19	-0.47	-0.49	-0.26	-0.43	0.08	-0.41	-0.28	-0.12	-0.34	-0.36	-0.05	-0.38	-0.11	1.00			
CSIL	0.41	0.54	0.61	0.54	0.40	0.56	0.10	0.47	0.38	0.11	0.40	0.35	0.61	0.22	-0.01	1.00		
FSAND	-0.49	-0.43	-0.67	-0.58	-0.60	-0.23	-0.50	-0.51	-0.43	-0.48	-0.57	-0.23	-0.63	-0.37	0.70	-0.20	1.00	
Cd	0.28	0.56	0.38	0.49	0.26	0.60	0.06	0.37	0.39	0.14	0.42	0.76	0.29	0.25	-0.18	0.49	-0.21	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.43

N = 21

Table 3.8: Summary and Significance of Correlations
Between Parameters in Lake and Rivers Stations

	r > 0.7		0.5 < r < 0.7		r < 0.5	
	Lake	Rivers	Lake	Rivers	Lake	Rivers
LOI	TKN,TOC,Sol,Fe,Mn,Pb,Zn	TKN,Sol,Mn,Pb,Zn,Cn,Cr	Cu,Cr,Hg,TP,Cd,PCB	Fe,Mn,Hg,PCB		TP,Cd
TP	Sol,PCB,Zn,Cu,Cr,Hg		TKN,Pb,Fe,Cr,Mn	Hg,Sol	TOC,LOI	TKN,LOI,Cu,Fe,Zn,Mn,Pb,Cr,PCB
TKN	TOC,LOI,Sol,Fe,Mn,Pb,Cd, Cr,Cu,Hg	Cu,LOI	PCB,TP	Cr,Pb,Sol,Zn		TP,Hg,Fe,Cd,Mn,PCB
TOC	TKN,LOI,Sol,Fe,Cu,Pb,Zn,Hg	*	PCB,Mn,Zn,Cr,Cd	*		*
Cu	TKN,TOC,Sol,Zn,Pb,Cr,Cd,Hg,TP	TKN,LOI,Sol,Pb,Zn,Cr,PCB	LOI,Fe,Mn	Hg,Fe,Mn		TP,Cd
Cr	TKN,Sol,Fe,Cu,Zn,TP,Hg, Pb,Cd,PCB	LOI,Sol,Fe,Mn,Pb,Zn,Cu	LOI,TOC,Mn	TKN,Hg		PCB,TP,Cd
Hg	TKN,TOC,Sol,Pb,Zn,Cu,Cr, Cd,Fe,TP,PCB	PCB,Sol,Zn,Pb	LOI,Mn	TP,Cu,Cr,Cd		Mn,Fe,TKN,TOC
Fe	TKN,LOIMn,Pb,Zn	Sol,Mn,Cr,Pb,Zn	PCB,Sol,TP,Cd,TOC	LOI,Cu		PCB,HG,TKN,TP,Cr
Pb	TOC,TKN,Sol,LOI,CU,Hg,Zn, Cd,Cr,Fe,PCB	LOI,Sol,Fe,Mn,Cu,Cr,An,Hg	TP,Mn	PCB,TKN		TP,Cd
Zn	TKN,TOC,LOI,Sol,Cu,Cr,Pb, Hg,TP,Fe,Cd,Mn,PCB	Sol,LOI,Cu,Pb,Cr,Hg,Fe, Mn,PCB		TKN		TP,Cd
Cd	TKN,Sol,Cu,Cr,Hg,Pb,Zn	PCB	LOI,TP,TOC,Fe,PCB	TP,Hg	Mn	LOI,TKN,Cu,Sol,Mn,Cr,Zn,Fe,Pb
Mn	TKN,LOI,Fe,Zn	LOI,Sol,Fe,Cr,Pb,Zn	TKN,TOC,Pb,Sol,TP,Cu,Hg	Cu	PCB,Cd	TP,TKN,Hg,PCB,Cd
Sol.	TKN,TOC,LOI,Pb,ZnHg,Cr,Cu,TP, Cd,PCB	LOI,Fe,Mn,Hg,Pb,Zn,Cu,Cr	Fe,Mn	TKN,PCB,Pb		TP,Cd
PCB	Cu,Cr,Pb,Zn,Hg,TP,Sol.	Cu,Hg,Zn,Cd	LOI,TKN,TOC,Fe,Cd	Pb,Sol	Mn	LOI,TP,TKN,Cr,Fe,Mn

* = No Data r > 0.7 (Significant Correlation) 0.5 < r < 0.7 (Good Correlation) r < 0.5 (Weak Correlation)

LOI, TKN and TOC are highly correlated in the lake stations. Since these parameters are indicative of the organic content of the sediment, they would be expected to show strong inter-relationships. The lake stations show a remarkable degree of relationship between most of the parameters. The underlying factor in this relationship appears to be the organic content of sediment, especially the solvent extractable parameter. Iron and manganese are highly correlated with each other in both the rivers and lake stations. This is reflective of their similar chemistry and widespread occurrence in nature (Dayal et al, 1983). Both of these metals are important "carrier particles" for other metals. However, only lead and zinc in the lake and rivers and chromium in the rivers, show a strong association with iron and manganese.

It appears that the organic "carrier particles" are more effective in adsorbing contaminants than iron and manganese which are themselves strongly associated with the organic fraction. (This will be discussed in further detail in the section under sequential extraction).

PCBs show a close relationship with solvent extractables and metals at the lake stations and to some extent in the river stations although the correlation between PCB and solvent extractables is weaker in the river stations.

In general, the interrelationships among parameters are stronger in the lake stations compared with the river stations. The hydrodynamics of the river system may be a major influence in the distribution of material in sediments.

As shown in Tables 3.6 and 3.7, most of the chemical parameters are associated with the silt and clay sediment fractions.

Correlation coefficients were also calculated for stations within the various study locations in an attempt to identify common sources of the parameters measured. In many cases, the number of stations were too small to provide firm conclusions. However, parameters at stations in the St. Marys River (Table 3.9) and the Toronto East Headland (Table

Table 3.9 Correlation Coefficients (r) for Parameters in Sediment - St. Mary's River

	% LOI	TP	TKN	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	FSAN	SAND	CSIL	SILT	CLAY
% LOI	1.00																
TP	0.61	1.00															
TKN	0.78	0.94	1.00														
Cu	0.86	0.89	0.92	1.00													
Cr	0.96	0.69	0.80	0.93	1.00												
Hg	0.91	0.85	0.92	0.98	0.96	1.00											
Fe	0.93	0.42	0.57	0.77	0.94	0.82	1.00										
Pb	0.96	0.71	0.84	0.94	0.97	0.94	0.89	1.00									
Zn	0.96	0.62	0.75	0.90	0.99	0.93	0.96	0.97	1.00								
Mn	0.89	0.31	0.47	0.69	0.89	0.74	0.99	0.84	0.93	1.00							
SOL	0.85	0.77	0.79	0.97	0.94	0.92	0.84	0.93	0.93	0.78	1.00						
PCB	0.72	0.71	0.76	0.87	0.78	0.81	0.68	0.82	0.82	0.63	0.87	1.00					
FSAN	-0.61	-0.95	-0.93	-0.89	-0.72	-0.86	-0.44	-0.76	-0.65	-0.34	-0.77	-0.72	1.00				
SAND	-0.54	-0.63	-0.62	-0.77	-0.64	-0.64	-0.50	-0.74	-0.65	-0.47	-0.81	-0.81	0.71	1.00			
CSIL	0.54	0.90	0.86	0.75	0.60	0.76	0.32	0.60	0.49	0.20	0.60	0.40	-0.88	-0.40	1.00		
SILT	0.58	0.96	0.94	0.84	0.65	0.81	0.35	0.70	0.56	0.24	0.70	0.61	-0.97	-0.63	0.95	1.00	
CLAY	0.84	0.35	0.54	0.61	0.83	0.76	0.88	0.73	0.83	0.85	0.60	0.49	-0.39	-0.16	0.35	0.30	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.75

N = 7

Table 3.10 Correlation Coefficients (r) for Parameters in Sediment - Toronto East Headland

	% LOI	TP	TKN	Cu	Cr	Hg	Fe	Pb	Zn	Mn	SOL	PCB	FSAN	SAND	CSIL	SILT	CLAY
% LOI	1.00																
TP	0.67	1.00															
TKN	0.99	0.71	1.00														
Cu	0.97	0.74	0.99	1.00													
Cr	0.90	0.85	0.93	0.96	1.00												
Hg	0.92	0.46	0.90	0.91	0.81	1.00											
Fe	0.96	0.70	0.97	0.98	0.94	0.92	1.00										
Pb	0.91	0.70	0.93	0.96	0.94	0.91	0.98	1.00									
Zn	0.94	0.73	0.96	0.99	0.95	0.90	0.95	0.96	1.00								
Mn	0.95	0.61	0.94	0.92	0.88	0.94	0.96	0.91	0.88	1.00							
SOL	0.68	0.36	0.69	0.62	0.56	0.58	0.72	0.61	0.52	0.77	1.00						
PCB	0.90	0.47	0.89	0.86	0.76	0.86	0.89	0.81	0.79	0.94	0.88	1.00					
FSAN	-0.83	-0.60	-0.81	-0.82	-0.84	-0.83	-0.78	-0.74	-0.79	-0.87	-0.49	-0.75	1.00				
SAND	-0.34	0.16	-0.21	-0.16	0.01	-0.45	-0.17	-0.14	-0.16	-0.30	-0.02	-0.24	0.27	1.00			
CSIL	0.48	0.72	0.55	0.66	0.75	0.49	0.64	0.72	0.71	0.50	0.19	0.39	-0.45	0.32	1.00		
SILT	0.90	0.53	0.90	0.93	0.86	0.97	0.91	0.91	0.93	0.93	0.57	0.87	-0.86	-0.28	0.63	1.00	
CLAY	0.90	0.79	0.94	0.97	0.99	0.84	0.96	0.97	0.96	0.89	0.60	0.79	-0.80	0.03	0.76	0.89	1.00

CRITICAL VALUE (2-tail, x < or = to 0.05) = +/- 0.70

N = 8

3.10) show a high degree of interrelationship suggesting that in addition to the parameter association with particular "carrier particles", there appears to be common sources of contaminants in each of the these two areas respectively.

3.2 Sediment-Sequential Extraction of Metals

Results of the sequential chemical extractions (on the <63 μm sediment) for each of the six geochemical phases (IW-interstitial water, F1-cation exchangeable, F2-easily reducible, F3-organic sulphide, F4-moderately reducible and Res-residual) are provided in Tables in Volume IV of this report series. The tables provide the concentrations of the metal (As, Zn, Cu, Cd, Mn, Fe, Pb) in each of the phases and the total metal concentrations which were obtained by summing the geochemical phases (i.e. TRSUM = IW + F1 + F2 + F3 + F4 + RES).

Table 3.11 provides a summary of the geochemical phases with the highest concentration of each metal. At most stations, As, Cd, Cu, Pb and Zn showed the highest concentrations in the F3 (organic/sulphide) phase. Manganese was concentrated in the F3 phase at about half of the stations and in the residual phase at the other half. Iron was found mainly in the residual phase.

3.2.1 Metal Distribution Among The Geochemical Phases Of Sediment

Summary statistics for the sequential extraction results for each of the study locations are provided in Tables 3.12-3.17. The information in the tables includes metals in each geochemical phase (average concentration and % of total metal), TRSUM (sum of individual phases) and potentially available metal (IW-F4) for each of the study locations. Arsenic will not be discussed in this section because of the small data set.

The proportion of metals in the various phases provides an indication of the influence of the different "carrier particles" in adsorbing metals. Metals in the residual phase are normally associated with detrital minerals, refractory organics and resistant sulphides (Tessier et al.,

TABLE 3.11: SUMMARY OF THE GEOCHEMICAL PHASES WITH THE HIGHEST METAL CONTENT

METAL	LARGEST LEVEL (L)	NO. OF STATIONS WITH L LARGER THAN OTHERS	TOTAL NO. OF STATIONS
AS	F3	32	40
CD	F3	73	87
CU	F3	77	87
FE	RES	69	87
PB	F3	84	87
MN	F3	44	87
	RES	43	
ZN	F3	74	87

Table: 3.12 Summary Statistics for Geochemical Distribution of Copper According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.050	0.026	8.480	4.482	0.002	0.001	131.224	69.353	31.388	16.589	171.144	90.451	18.068	9.549	189.212
O/S HAMIL. HARBOUR	0.020	0.062	4.106	12.767	0.002	0.006	20.874	64.903	2.922	9.085	27.924	86.823	4.238	13.177	32.162
HUMBER BAY	0.047	0.033	3.882	2.702	0.047	0.033	104.212	72.531	12.525	8.717	120.071	83.569	22.951	15.974	143.679
TORONTO HARBOUR	0.043	0.060	2.632	3.690	0.002	0.003	46.602	65.327	3.245	4.549	52.524	73.629	18.812	26.371	71.336
EASTHEADLAND	0.009	0.010	0.211	0.237	1.596	1.792	63.107	70.852	6.017	6.755	70.931	79.636	18.120	20.344	89.069
ASHBRIDGES BAY	0.041	0.024	5.570	3.205	0.002	0.001	87.600	50.408	19.170	11.031	112.383	64.669	61.400	35.331	173.783
TOR. E. WATERFRONT	0.026	0.110	3.597	15.216	0.002	0.008	10.508	44.452	1.064	4.501	15.196	64.284	8.440	35.704	23.639
FRENCHMAN BAY	0.009	0.016	9.882	17.192	0.002	0.003	32.924	57.278	8.476	14.746	51.293	89.235	6.188	10.765	57.481
ST.CLAIR RIVER	0.005	0.015	0.394	1.175	0.085	0.254	25.891	77.231	1.197	3.571	27.567	82.231	5.950	17.748	33.524
NIAGARA RIVER	0.005	0.006	0.094	0.106	0.158	0.178	72.360	81.300	3.189	3.583	75.800	85.165	13.195	14.825	89.004
ST. MARY'S RIVER	0.005	0.006	0.263	0.306	0.187	0.218	61.058	71.017	4.824	5.611	66.330	77.149	19.631	22.833	85.976
ST. LAWRENCE RIVER	0.005	0.014	0.109	0.304	0.109	0.304	24.456	68.294	2.847	7.950	27.522	76.856	8.277	23.114	35.810

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.13 Summary Statistics for Geochemical Distribution of Cadmium According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW -F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.010	0.086	0.490	4.205	0.768	6.590	6.204	53.235	1.760	15.102	9.232	79.217	2.422	20.783	11.654
O/S HAMIL. HARBOUR	0.007	0.172	0.236	5.811	0.648	15.957	1.350	33.243	0.374	9.210	2.615	64.393	1.446	35.607	4.061
HUMBER BAY	0.013	0.123	0.184	1.745	0.452	4.287	7.184	68.134	0.889	8.431	8.721	82.711	1.794	17.014	10.544
TORONTO HARBOUR	0.013	0.152	0.284	3.320	0.396	4.629	4.846	56.645	0.949	11.093	6.488	75.839	2.067	24.161	8.555
EASTHEADLAND	0.008	0.474	0.030	1.777	0.030	1.777	1.492	88.389	0.098	5.806	1.658	98.223	0.030	1.777	1.688
ASHBRIDGES BAY	0.008	0.109	0.250	3.414	0.445	6.077	3.965	54.144	0.390	5.326	5.058	69.070	2.265	30.930	7.323
TOR. E. WATERFRONT	0.008	0.176	0.222	4.896	0.430	9.484	1.527	33.679	0.179	3.948	2.365	52.161	2.169	47.839	4.534
FRENCHMAN BAY	0.005	0.062	0.418	5.151	1.274	15.699	3.840	47.320	0.674	8.306	6.211	76.537	1.904	23.463	8.115
ST.CLAIR RIVER	0.003	0.301	0.045	4.514	0.050	5.015	0.643	64.493	0.049	4.915	0.792	79.438	0.205	20.562	0.997
NIAGARA RIVER	0.003	0.086	0.052	1.486	0.052	1.486	3.253	92.969	0.086	2.458	3.447	98.514	0.052	1.486	3.499
ST. MARY'S RIVER	0.003	0.241	0.055	4.425	0.055	4.425	1.006	80.933	0.066	5.310	1.188	95.575	0.055	4.425	1.243
ST. LAWRENCE RIVER	0.003	0.232	0.066	5.112	0.066	5.112	0.968	74.981	0.066	5.112	1.171	90.705	0.120	9.295	1.291

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.14 Summary Statistics for Geochemical Distribution of Lead According to Study Locations

Location	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIw - F4)		Residual		Total
	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	$\bar{X}$	%	($\Sigma\bar{X}$)
WINDERMERE BASIN	0.055	0.014	3.156	0.824	9.338	2.437	277.700	72.481	7.288	1.902	297.897	77.752	85.240	22.248	383.137
D/S HAMIL. HARBOUR	0.005	0.007	1.626	2.237	7.056	9.706	45.900	63.137	2.812	3.868	57.399	78.954	15.300	21.046	72.699
HUMBER BAY	0.021	0.010	3.075	1.455	4.989	2.361	186.625	88.321	4.403	2.084	199.112	94.231	11.972	5.666	211.303
TORONTO HARBOUR	0.047	0.014	4.344	1.282	6.725	1.985	243.490	71.859	3.049	0.900	257.655	76.039	81.190	23.961	338.845
EASTHEADLAND	0.025	0.013	0.858	0.448	3.233	1.688	173.852	90.789	9.683	5.057	187.652	97.995	3.820	1.995	191.491
ASHBRIDGES BAY	6.039	0.010	5.445	1.440	7.415	1.962	277.250	73.344	1.815	0.480	291.964	77.236	86.050	22.764	378.014
TOR. E. WATERFRONT	0.015	0.019	3.810	4.822	4.849	6.137	52.886	66.930	0.976	1.235	62.505	79.104	16.511	20.896	79.016
FRENCHMAN BAY	0.018	0.011	5.502	3.272	14.024	8.341	123.320	74.536	4.190	2.492	149.054	88.652	19.080	11.348	168.134
ST.CLAIR RIVER	0.025	0.036	0.376	0.545	0.376	0.545	66.042	95.714	0.686	0.994	67.505	97.835	1.482	2.148	68.999
NIAGARA RIVER	0.025	0.023	0.430	0.398	0.430	0.398	100.468	92.973	3.039	2.812	104.392	96.605	3.651	3.379	108.061
ST. MARY'S RIVER	0.020	0.012	0.647	0.402	0.647	0.402	141.611	87.930	8.736	5.424	151.665	94.173	9.344	5.802	161.049
ST. LAWRENCE RIVER	0.025	0.102	0.546	2.231	0.546	2.231	21.822	89.175	0.546	2.231	23.485	95.971	0.956	3.907	24.471

$\bar{X}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{X}$)

Table: 3.15 Summary Statistics for Geochemical Distribution of Zinc According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	($\Sigma\bar{I}$)
WINDERMERE BASIN	0.590	0.041	11.488	0.807	27.898	1.960	1008.880	70.868	292.560	20.551	1341.416	94.227	82.180	5.773	1423.596
O/S HAMIL. HARBOUR	0.094	0.058	4.882	3.033	8.582	5.332	97.060	60.309	6.320	3.927	116.938	72.660	44.000	27.340	160.938
HUMBER BAY	0.073	0.012	3.428	0.563	8.705	1.429	467.190	76.682	39.541	6.490	518.925	85.174	90.554	14.863	609.254
TORONTO HARBOUR	0.133	0.032	2.426	0.587	8.578	2.077	340.910	82.555	12.252	2.967	364.299	88.219	48.650	11.781	412.949
EASTHEADLAND	0.006	0.002	0.910	0.334	5.898	2.162	144.763	53.076	34.672	12.712	186.334	68.317	86.409	31.681	272.748
ASHBRIDGES BAY	0.027	0.005	4.315	0.726	8.860	1.491	392.950	66.116	13.135	2.210	419.287	70.547	175.050	29.453	594.337
TOR. E. WATERFRONT	0.022	0.023	2.017	2.089	3.832	3.968	46.222	47.867	1.114	1.154	53.207	55.101	43.356	44.899	96.563
FRENCHMAN BAY	0.040	0.020	1.900	0.957	4.890	2.464	123.340	62.145	2.740	1.381	132.912	66.968	65.560	33.032	198.472
ST.CLAIR RIVER	0.003	0.002	0.872	0.651	1.441	1.076	95.316	71.140	4.741	3.538	102.370	76.405	31.698	23.658	133.984
NIAGARA RIVER	0.003	0.001	1.397	0.352	7.494	1.889	257.163	64.841	22.110	5.574	288.187	72.657	108.454	27.343	396.639
ST. MARY'S RIVER	0.011	0.003	2.722	0.621	38.811	8.848	307.493	70.102	18.633	4.248	367.689	83.825	70.938	16.172	438.638
ST. LAWRENCE RIVER	0.011	0.010	0.421	0.401	0.713	0.680	51.621	49.228	6.562	6.258	59.328	56.577	45.521	43.410	104.862

$\bar{I}$ - Mean Concentration (ppm)
I - % of Total Metal (i.e. $\Sigma\bar{I}$)

Table: 3.16 Summary Statistics for Geochemical Distribution of Manganese According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{I}$	%	$\bar{I}$	%	$\bar{I}$	%	$\bar{I}$	%	$\bar{I}$	%	$\bar{I}$	%	$\bar{I}$	%	($\Sigma\bar{I}$)
WINDERMERE BASIN	2.248	0.359	11.038	1.762	264.060	42.154	251.478	40.146	68.788	10.981	597.612	95.402	28.800	4.598	626.412
O/S HAMIL. HARBOUR	14.096	2.246	15.698	2.501	275.720	43.929	281.022	44.774	22.070	3.516	608.606	96.966	19.004	3.028	627.646
HUMBER BAY	2.836	0.602	17.459	3.703	65.609	13.917	196.478	41.677	25.757	5.464	308.160	65.367	163.153	34.608	471.428
TORONTO HARBOUR	3.265	0.676	3.917	0.811	62.679	12.978	170.325	35.268	11.505	2.382	251.691	52.115	231.260	47.885	482.951
EASTHEADLAND	1.148	0.175	45.560	6.962	80.185	12.254	254.363	38.871	43.043	6.578	424.298	64.840	229.199	35.026	654.374
ASHBRIDGES BAY	3.705	0.788	2.450	0.521	23.715	5.042	161.455	34.329	8.995	1.913	200.320	42.592	270.000	57.408	470.320
TOR. E. WATERFRONT	2.793	0.567	1.694	0.344	32.747	6.645	102.351	20.770	9.899	2.009	149.484	30.335	343.289	69.665	492.773
FRENCHMAN BAY	3.686	0.721	5.268	1.030	128.928	25.202	255.546	49.952	14.974	2.927	408.402	79.831	103.180	20.169	511.582
ST.CLAIR RIVER	0.728	0.201	11.627	3.204	35.468	9.773	213.898	58.939	11.507	3.171	273.228	75.287	89.363	24.624	362.914
NIAGARA RIVER	1.612	0.322	27.581	5.515	76.038	15.204	175.169	35.026	14.257	2.851	294.657	58.918	204.046	40.800	500.117
ST. MARY'S RIVER	0.598	0.059	49.549	4.877	62.127	6.115	82.645	8.134	23.202	2.284	228.120	22.452	786.642	77.423	1016.028
ST. LAWRENCE RIVER	0.041	0.011	11.791	3.063	40.672	10.567	105.789	27.485	9.816	2.550	168.107	43.676	216.738	56.311	384.898

$\bar{I}$ - Mean Concentration (ppm)
% - % of Total Metal (i.e. $\Sigma\bar{I}$)

Table: 3.17 Summary Statistics for Geochemical Distribution of Iron According to Study Locations

Study Locations	IW		F1		F2		F3		F4		Potentially Available Metal (ΣIW - F4)		Residual		Total
	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	$\bar{I}$	I	($\Sigma\bar{I}$)
WINDERMERE BASIN	2.830	0.018	28.000	0.181	774.550	4.997	7109.000	45.864	0.000	0.000	3130.410	20.196	7585.800	48.940	15500.170
O/S HAMIL. HARBOUR	2.520	0.013	5.490	0.028	223.770	1.155	3544.600	18.300	0.000	0.000	891.980	4.605	15593.200	80.504	19369.590
HUMBER BAY	1.290	0.005	7.000	0.029	107.468	0.444	6429.995	26.583	588.111	2.431	7133.862	29.493	17054.964	70.508	24188.644
TORONTO HARBOUR	2.160	0.016	3.770	0.028	98.600	0.731	7164.100	53.103	0.000	0.000	2923.030	21.666	6222.400	46.122	13491.030
EASTHEADLAND	0.100	0.000	0.450	0.001	142.488	0.421	6827.429	20.175	1665.584	4.922	8636.056	25.519	25205.675	74.481	33841.753
ASHBRIDGES BAY	1.260	0.011	3.220	0.028	34.660	0.300	4722.500	40.822	0.000	0.000	823.500	7.118	6807.000	58.840	11568.630
TOR. E. WATERFRONT	0.430	0.002	1.200	0.007	34.360	0.199	3053.330	17.724	0.000	0.000	1832.350	10.636	14138.110	82.067	17227.420
FRENCHMAN BAY	1.710	0.006	5.580	0.021	118.280	0.435	12531.800	46.098	0.000	0.000	5073.810	18.664	14527.600	53.440	27184.970
ST.CLAIR RIVER	0.320	0.002	1.938	0.013	97.966	0.666	4159.542	28.297	516.242	3.512	4776.013	32.491	10082.866	68.594	14699.357
NIAGARA RIVER	12.570	0.039	0.200	0.001	193.000	0.602	6549.300	20.430	631.100	1.969	7386.200	23.041	22731.900	70.912	32056.600
ST. MARY'S RIVER	0.090	0.000	4.091	0.006	504.843	0.791	5875.142	9.210	1195.853	1.875	7580.014	11.883	56208.450	88.117	63788.641
ST. LAWRENCE RIVER	0.010	0.000	2.695	0.011	25.397	0.100	4115.364	16.132	680.857	2.669	4824.325	18.912	20685.444	81.088	25509.794

$\bar{I}$ - Mean Concentration (ppm)
I - % of Total Metal (i.e. $\Sigma\bar{I}$)

1979). Metals in this phase are chemically stable under normal environmental conditions and can be considered biologically unavailable. The potentially available metal (IW-F4) can be considered to have originated mainly from anthropogenic sources (Tessier, et al., 1979). Table 3.12 shows the geochemical distribution of copper (Cu) among the study locations. For most areas, over 75% of the Cu was in potentially available forms. The two exceptions were Ashbridges Bay and Eastern Toronto Waterfront where 35% was in the residual form. Most of the Cu outside the residual phase was associated with the F3 (organic/sulphide fraction) phase. Concentrations in the IW and F2 phases were negligible. The F1 (cation exchangeable) phase showed appreciable amounts of Cu in sediment from Eastern Toronto Waterfront, outside Hamilton Harbour and Frenchman Bay. This phase consists of the easily available fraction which is in dynamic equilibrium with the surrounding water. The F4 (moderately reducible, Fe/Mn oxyhydroxide fraction) phase contained significant amounts of Cu, suggesting that next to organic material, the metal hydrous oxides are the most important "carrier particles" for copper.

Over 90% of the cadmium (Cd) in the St. Marys River, St. Lawrence River and Niagara River and the East Toronto Headland was in potentially available forms. The lowest value of available cadmium was noted for sediment from Eastern Toronto Waterfront, where almost 50% was bound up in the residual fraction (Table 3.13). Appreciable amounts of cadmium were noted in the F1, F2 and F4 phases, but the bulk of the available Cd was in the F3 phase (organic/sulphide fraction).

More than 75% of lead (Pb) was in the potentially available forms for all stations (Table 3.14). In Humber Bay, Toronto East Headland and the interconnecting channels, over 90% of the Pb was in available forms. Most of the available Pb was associated with the F3 phase (organic/sulphide fraction) with extremely low levels in the other available (non-residual) fractions.

A significant proportion of the zinc (Zn) in the St. Lawrence River and Eastern Toronto Waterfront sediments was bound up in the residual fraction (Table 3.15). In general, most of the Zn was associated with

the F3 phase. However, at the Toronto East Headland and Windermere Basin appreciable amounts of Zn were associated with the Fe/Mn oxyhydroxide phase. Zinc concentrations in the other non-residual phases were negligible.

Over 50% of the manganese (Mn) in Ashbridges Bay, Eastern Toronto Waterfront, St. Marys River and St. Lawrence River was concentrated in the residual phase (Table 3.16). Toronto Harbour and Niagara River also showed significant proportions (40%) of Mn in the residual phase. Unlike the metals discussed earlier, a considerable proportion of Mn was found in the F2 phase (easily reducible fraction) which represents mainly the Mn oxyhydroxides. Only the St. Clair River sediments had more than 50% Mn in the F3 phase.

The bulk of Fe was found in the residual phase, with most of the available Fe in the F3 phase.

With the exception of Fe and Mn, most of the potentially available metals were concentrated in the F3 phase (organic/sulphide fraction). This information agrees quite well with the results obtained through the correlation matrix on the bulk chemistry data, where good correlations were noted between the metals and the organic matter content of sediment and poor correlations between the other metals and Fe and Mn.

Fine organic matter has a large surface area to volume ratio and can therefore, in proportion to its volume, adsorb considerably greater amounts of metals. In addition, the other non-residual "carrier particles" appeared to be themselves associated with the organic/sulphide fraction, making this fraction the most important geochemical phase with which the metals were associated.

The largest fraction of Fe and to some extent Mn, was held in the residual phase. The sediments of Eastern Toronto Waterfront showed higher residual values for most metals compared with sediments from other locations, perhaps due to the lower organic matter content and higher mineral content of sediments from this area.

With the exception of Fe and Mn, most of the metals are in potentially available forms. Release from sediments however, will depend on changes in the physico-chemical factors (Eh, pH) which regulate the metal chemistry.

3.3 Biological Results

Of the 87 stations sampled during the 1983 survey, sediment from 49 stations provided adequate amounts of benthic tissue for chemical analyses. At 42 of the 49 stations, oligochaetes were the predominant group of organisms found and was comprised mainly of Limnodrilus hoffmeisteri and Tubifex tubifex. At the other 7 stations where adequate amounts of benthic tissue were obtained, there were abundances of organisms other than oligochaetes. These included mayfly nymphs at stations 50 and 51 in the upper St. Marys River (Figure 2.8) and station 64 in the St. Clair River (Figure 2.9); amphipods at stations 356 and 357 in the St. Lawrence River (Figure 2.11); chironomids at station 360 in the St. Lawrence River and station 2084 on the Eastern Toronto Waterfront (Figure 2.6).

Sufficient biomass for chemical analysis could not be obtained at 38 stations because of one or more of the following:

1. The substrate was unsuitable (e.g. sandy substrate) as benthic habitat. As a result, benthic densities were low.

2. There were high diversities and low densities of organisms which made it difficult to obtain enough organisms from any one taxon for analysis.

3. In areas where the sediment was high in organic matter, the organic debris created difficulties in sieving by clogging the mesh of the sieve. This, coupled with low organism density made sorting of the organisms difficult.

4. Certain areas were devoid of organisms, possibly the result of toxic bottom conditions since the sediment from these areas showed high levels of chemical contamination.

Chemical analyses for metals, PCBs and organochlorine pesticides (PCB/OC) required approximately 10 - 15 gms of tissue. When less than 10 gms were obtained, analyses were carried out first for the metals (except Hg), then Hg followed by PCB/organochlorine pesticides (scan). Based on this scheme, data on metal levels in oligochaetes were obtained at 42 stations, Hg at 38 and PCB/OC at 22 stations.

Arsenic was not included on the initial list of metals to be analyzed but was introduced during the late stages of the Phase 1 studies . As a result, data on arsenic levels in benthic tissue were only obtained for 10 stations. Detectable levels of the other metals were obtained at all stations for which analyses were carried out (summary statistics are provided in Table 3.18). Among the pesticides; DDT, mirex, heptachlor epoxide, dieldrin, endrin and the endosulfan isomers were not detected in benthic tissue. Summary statistics for PCBs and the pesticides that bioaccumulated in benthic tissue are provided in Table 3.19.

3.3.1 The Relationship Between Contaminant Levels in Benthic Organisms and Sediment

3.3.1.1 PCBs and Organochlorine Pesticides.

Table 3.20 shows the levels of PCB and pesticides in benthic tissue and sediment and the ratio of the tissue/sediment values referred to as bioconcentration factors.

Significant bioaccumulation of pesticides by oligochaetes were noted at certain locations. These included stations in the vicinity of the Toronto Main Sewage Treatment Plant outfall (2101, 2102 and 2103, Figure 2.5); Toronto Harbour (1346, 1352, 1354, 1362, 1365, 1366 and 1379, Figure 2.4); Humber Bay (2330, 2331, 2334, 2335 and 2369, Figure 2.3) and one station directly outside Hamilton Harbour (2097, Figure 2.2).

The sediment from these stations showed very low levels of pesticides and in many cases, levels were below analytical detection limits (a value of half the detection limits has been substituted in these cases).

TABLE 3.18: SUMMARY STATISTICS FOR METALS IN BENTHIC TISSUE (µg/g, dry wt.)

PARAMETERS	MEAN	STANDARD DEVIATION	MINIMUM	MAXIMUM
As	5.3	7.4	0.7	21.6
Cd	0.3	0.2	0.1	1.2
Cu	36.1	19.9	9.6	82.0
Fe	3498.4	7065.9	104.2	41655.7
Hg	0.3	0.1	0.1	0.5
Mn	31.5	35.7	1.2	183.7
Pb	9.5	16.0	0.1	60.6
Zn	216.3	128.0	62.9	663.4

TABLE 3.19: SUMMARY STATISTICS FOR PCB AND PESTICIDES IN BENTHIC TISSUE (ng/g, dry wt.)

PARAMETERS	MEAN	STANDARD DEVIATION	MINIMUM	MAXIMUM
DDD	135.12	135.11	38.70	459.40
Chlordane	78.29	45.28	9.52	193.20
Lindane	48.62	43.29	9.71	147.23
A-BHC	28.94	22.20	9.69	106.27
DDE	119.57	69.65	58.39	328.90
Aldrin	47.36	53.17	16.43	204.37
Heptachlor	32.87	39.90	12.85	158.95
HCB	116.62	101.47	26.06	453.44
PCB	1030.00	640.00	130.00	1970.00

Table 3.20 PCB and Pesticides Residues in Sediment And Benthic Tissue
And Bioconcentration Factors (ratio of Benthic Tissue conc./Sediment conc.)

Station	** PCB **			** PP.DDD **			** ALDRIN **		
	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF
1346	1300	1450	1	46.00	459.40	10	0.50	38.86	78
1352	590	1330	2	2.50	38.70	15	0.50	25.81	52
1354	350	1150	3	--	--	--	--	--	--
1357	150	1090	7	--	--	--	--	--	--
1362	110	580	5	2.50	68.45	27	--	--	--
1365	120	1140	10	2.50	138.94	56	0.50	25.85	52
1366	180	1470	8	20.00	124.52	6	0.50	29.22	58
1371	290	120	0	--	--	--	--	--	--
1379	30	260	9	--	--	--	--	--	--
2034	300	700	2	--	--	--	--	--	--
2082	10	260	26	--	--	--	--	--	--
2083	10	130	13	--	--	--	--	--	--
2089	1010	1640	2	--	--	--	--	--	--
2090	3090	1320	0	--	--	--	--	--	--
2097	10	1810	181	--	--	--	0.50	16.43	33
2101	10	250	25	--	--	--	--	--	--
2102	10	320	32	--	--	--	--	--	--
2103	10	1530	153	--	--	--	0.50	204.37	409
2330	190	1520	8	2.50	99.81	40	0.50	38.64	77
2331	120	1780	15	20.00	90.08	5	0.50	45.10	90
2334	30	1710	57	2.50	61.05	24	0.50	22.49	45
2335	30	1970	66	--	--	--	0.50	51.59	103
2369	--	--	--	--	--	--	0.50	22.63	45

-- Not Detected in Benthic Organisms

Bioconcentration Factors (BCF) Were Rounded Off To The Nearest Whole Number

Table 3.20 (cont'd) PCB and Pesticides Residues in Sediment And Benthic Tissue And Bioconcentration Factors (ratio of Benthic Tissue)

Station	** LINDANE **			** HCB **			** PP,DDE **		
	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF
1346	0.50	9.71	19	2.00	42.09	21	0.50	74.50	147
1352	0.50	16.13	32	0.50	68.17	136	0.50	87.13	174
1354	0.50	75.02	150	--	--	--	--	--	--
1357	--	--	--	2.00	26.06	13	0.50	65.23	130
1362	0.50	78.28	157	0.50	104.37	209	--	--	--
1365	--	--	--	0.50	67.86	136	0.50	84.02	168
1366	--	--	--	0.50	81.17	162	0.50	129.88	260
1371	--	--	--		--	--	--	--	--
1379	--	--	--	1.00	42.38	42	--	--	--
2034	0.50	52.38	105	0.50	288.13	576	--	--	--
2082	0.50	19.76	40		--	--	--	--	--
2083	0.50	19.71	39		--	--	--	--	--
2089	--	--	--	0.50	38.75	78	0.50	67.82	136
2090	--	--	--	0.50	109.21	218	0.50	86.36	173
2097	--	--	--	0.50	157.86	316	96.00	213.78	2
2101	0.50	55.05	110	0.50	453.44	907	--	--	--
2102	0.50	147.23	294	0.50	55.61	111	0.50	98.15	196
2103	0.50	12.97	26	0.50	123.27	247	0.50	58.39	117
2330	--	--	--	3.00	80.49	27	5.00	132.00	26
2331	--	--	--	0.50	83.77	168	0.50	128.87	258
2334	--	--	--	0.50	154.32	309	--	--	--
2335	--	--	--	0.50	148.32	297	--	--	--
2369	--	--	--	0.50	90.53	181	--	--	--

-- Not Detected in Benthic Organisms

Bioconcentration Factors (BCF) Were Rounded Off To The Nearest Whole Number

Table 3.20 (cont'd) PCB and Pesticides Residues in Sediment And Benthic Tissue
And Concentration Factors (ratio of Benthic Tissue)

Station	** A-BHC **			** CHLORDANE **			** HEPTACHLOR **		
	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF	Sediment (ng/g dry wt.)	Benthic Tissue Corrected For Gut Content (ng/g dry wt.)	BCF
1346	0.50	12.95	26	8.00	106.80	13	0.50	25.91	52
1352	0.50	25.81	52	2.00	80.66	40	0.50	19.36	39
1354	0.50	16.30	33	2.00	45.63	23	0.50	78.28	157
1357	--	--	--	--	--	--	0.50	13.04	26
1362	0.50	16.30	33	2.00	88.03	44	--	--	--
1365	0.50	19.39	39	2.00	77.54	39	0.50	16.15	32
1366	0.50	19.48	39	16.00	84.19	5	0.50	19.48	39
1371	--	--	--	--	--	--	--	--	--
1379	0.50	19.56	39	2.00	32.58	16	--	--	--
2034	--	--	--	--	--	--	--	--	--
2082	--	--	--	--	--	--	--	--	--
2083	--	--	--	--	--	--	--	--	--
2089	--	--	--	18.50	9.52	0	--	--	--
2090	0.50	22.48	45	--	--	--	0.50	12.85	26
2097	0.50	36.17	72	--	--	--	0.50	13.14	26
2101	0.50	25.90	52	2.00	25.89	13	--	--	--
2102	0.50	35.98	72	2.00	85.03	43	--	--	--
2103	0.50	32.43	65	2.00	100.54	50	0.50	158.95	318
2330	0.50	106.27	213	2.00	193.20	97	0.50	19.32	39
2331	0.50	12.88	26	11.00	128.80	12	0.50	19.33	39
2334	0.50	41.78	84	4.00	57.83	14	0.50	25.71	51
2335	0.50	38.69	77	--	--	--	0.50	25.79	51
2369	0.50	9.69	19	9.00	58.11	6	0.50	12.93	26

-- Not Detected in Benthic Organisms

Bioconcentration Factors (BCF) Were Rounded Off To The Nearest Whole Number

A common characteristic of several of the stations at which pesticide bioaccumulation by oligochaetes was noted, was their proximity to discharges. The station outside Hamilton Harbour is influenced by discharges from the Harbour; the Humber Bay stations are influenced by discharges from the Humber River, Mimico Creek, the Humber STP and storm sewers (Figure 3.2); stations in Toronto Harbour are influenced by various storm sewers (Figure 3.2) and the Don River. Stations 2101, 2102 and 2103 are in close proximity to the Toronto Main STP discharge.

The detection of several pesticides in biota and the proximity of the stations to discharge sources suggest that although the concentrations of these pesticides in sediment were low, there may be continuous inputs of low levels of these pesticides which accumulate in the tissues of benthic organisms that feed on the incoming material. This aspect will be addressed in the discussion section that follows.

3.3.1.2 Metals

Table 3.21 shows the level of metals in sediment and biota and the respective bioconcentration factors. The sediment metal values used in these tables were the "available" metal concentrations (IW-F4) obtained from the sequential extraction data. The stations where biota bioconcentrated contaminants are shown in Figure 3.3.

Manganese (Mn), cadmium (Cd) and lead (Pb) levels were extremely low in benthic tissues compared with the sediment values. In some cases, the Pb levels in benthic tissue were so low that gut correction resulted in negative values (Table 3.21). This would indicate that most of the wet weight values for Pb in biota were associated with the sediment of the gut.

The levels of copper in benthic tissue exceeded the levels in sediment at 15 of the 42 stations (i.e. concentration factors >1).

Among the biologically essential metals, Zn showed the highest uptake values relative to sediment levels. The body burden values showed wide variation ranging from 62 ppm to 671 ppm, with 90% of the samples

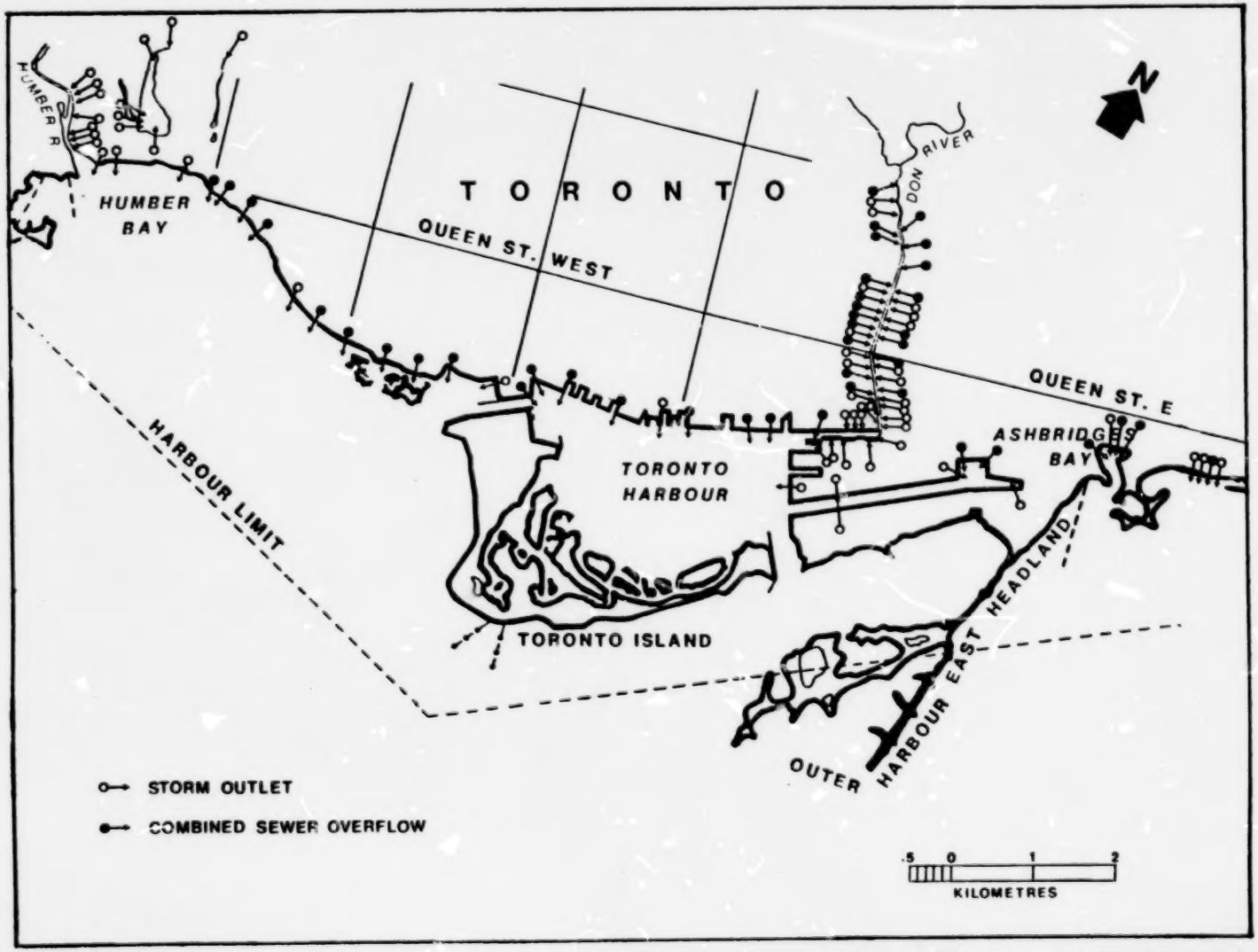

FIGURE 3.2 : MAP SHOWING STORM OUTLETS AND COMBINED SEWER OVERFLOWS INTO LAKE ONTARIO AND OPEN WATER COURSES

Table 3.21: Concentrations of Metal in Sediment(p.p.m.,dry weight) and in Benthic Tissue(p.p.m.,dry weight gut corrected) - Copper, Zinc, Lead, Cadmium

Location	Station	Copper			Zinc			Lead			Cadmium		
		Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF
Wincermere Basin	2085	272.2	29.1	0.1	2216.4	142.2	0.1	368.0	-4.2‡	0.0	14.9	0.2	0.0
	2094	245.7	42.2	0.2	1956.7	207.4	0.1	194.8	1.3	0.0	14.0	0.3	0.0
Outside Har. Hbr.	2097	23.7	44.5	1.9	146.2	547.2	3.7	60.0	-0.5‡	0.0	2.7	0.1	0.1
Humber Bay	2113	161.6	22.5	0.1	350.9	125.0	0.4	287.8	6.8	0.0	6.8	0.2	0.0
	2115	427.6	19.9	0.0	1737.6	71.8	0.0	311.5	0.3	0.0	57.3	-0.2‡	0.0
	2118	161.5	48.8	0.3	442.0	227.8	0.5	244.4	8.5	0.0	12.6	1.1	0.1
	2330	28.2	34.2	1.2	566.5	147.8	0.3	206.7	0.0	0.0	11.4	0.2	0.0
	2331	113.6	24.6	0.2	578.5	144.7	0.3	224.1	-0.3‡	0.0	13.3	0.2	0.0
	2334	46.1	21.8	0.5	145.2	154.1	1.1	88.1	0.7	0.0	3.9	0.3	0.1
	2335	54.3	82.0	1.5	334.1	408.8	1.2	174.9	0.1	0.0	8.1	0.2	0.0
	2369	67.6	21.2	0.3	496.9	97.5	0.2	241.4	-1.8‡	0.0	9.2	0.2	0.0
	2370	332.1	19.6	0.1	1354.8	91.9	0.1	245.2	0.4	0.0	47.1	-0.2‡	0.0
	2371	121.5	20.7	0.2	531.7	189.8	0.4	245.5	9.9	0.0	10.9	0.2	0.0
Toronto Harbour	1348	60.1	24.4	0.4	471.5	195.0	0.4	460.7	-6.0‡	0.0	9.2	0.2	0.0
	1350	76.8	42.7	0.6	437.6	210.7	0.5	324.8	-1.8‡	0.0	9.1	0.2	0.0
	1354	34.1	42.1	1.3	462.5	245.3	0.5	284.0	54.6	0.2	5.7	0.1	0.0
	1357	71.4	33.7	0.5	401.4	182.4	0.5	420.0	13.1	0.0	9.4	0.2	0.0
	1362	45.4	58.5	1.3	367.5	261.0	0.7	170.2	47.5	0.3	5.4	0.2	0.0
	1365	62.4	31.0	0.5	330.4	239.0	0.7	306.9	4.2	0.0	8.0	0.2	0.0
	1366	73.5	50.0	0.7	431.9	283.0	0.7	226.1	10.4	0.0	8.2	0.2	0.0
	1371	49.7	79.1	1.6	356.3	239.7	0.7	156.3	41.5	0.3	5.7	0.2	0.0
	1376	31.1	37.4	1.2	249.7	191.8	0.8	108.3	-2.5‡	0.0	1.2	0.2	0.2
Eastern Headland	2108	48.1	54.4	1.1	99.6	663.4	6.6	116.4	12.6	0.1	2.1	1.1	0.5
	2277	87.6	77.2	0.9	257.9	456.5	1.8	242.9	20.4	0.1	4.7	0.5	0.1
	2281	56.6	70.1	1.2	143.6	463.3	3.2	164.3	26.0	0.2	2.6	1.2	0.5
	2284	105.6	55.3	0.5	333.0	325.5	1.0	307.0	26.3	0.1	4.5	0.2	0.1
	2273	53.8	30.1	0.6	97.4	285.2	2.9	107.7	3.3	0.3	1.2	0.2	0.2
Ashbridges Bay	2034	72.9	34.6	0.5	401.3	239.0	0.6	315.3	-8.7‡	0.0	3.9	0.2	0.1
E. Tor. Waterfront	2101	11.1	15.7	1.4	25.9	135.2	5.2	34.4	0.5	0.0	2.1	0.3	0.1
	2102	16.9	76.8	4.5	59.3	207.6	3.5	66.2	-0.8‡	0.0	2.6	0.2	0.1
	2103	14.6	15.6	1.1	40.3	116.4	2.9	44.8	0.2	0.0	2.1	0.3	0.1
	2082	13.4	41.0	3.1	31.1	232.7	7.5	35.8	-0.1‡	0.0	2.0	0.2	0.1
	2083	16.9	25.2	1.5	48.6	62.9	1.3	103.4	-1.4‡	0.0	2.5	0.2	0.1
St. Clair River	66	22.3	9.6	0.4	43.3	82.2	1.9	20.2	2.7	0.1	0.8	0.3	0.4
Niagara River	113	99.3	54.3	0.5	209.9	282.6	1.3	187.1	60.6	0.3	4.3	0.2	0.0
	157	77.9	15.5	0.2	97.9	165.7	1.7	156.6	-1.3‡	0.0	4.1	0.2	0.0
	160	18.6	12.9	0.7	125.9	131.1	1.0	27.1	2.5	0.1	0.9	0.3	0.3
	183	131.7	19.7	0.1	687.8	164.5	0.2	165.2	-1.5‡	0.0	5.4	0.2	0.0
St. Marys River	45	23.1	22.5	1.0	118.7	131.3	1.1	58.4	2.4	0.0	1.0	0.3	0.3
	46	166.9	24.0	0.1	730.3	115.8	0.2	217.4	0.2	0.0	3.5	0.3	0.1
	47	89.4	11.4	0.1	493.8	107.5	0.2	157.1	1.2	0.0	2.0	0.3	0.2
	48	168.1	17.0	0.1	947.3	110.7	0.1	619.3	6.6	0.0	4.5	0.3	0.1

‡ See Text For Explanation Regarding Negative Values

BCF = Bioconcentration Factors (Contaminant concentration in benthic tissue/contaminant concentration in sediment)

Table 3.21 cont'd: Concentrations of Metal in Sediment(p.p.m.,dry weight) and in Benthic Tissue(p.p.m.,dry weight gut corrected) - Iron, Manganese, Mercury

Location	Station	Iron			Manganese			Mercury			Arsenic		
		Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF	Sediment	Benthic Tissue	BCF
Windermere Basin	2089	6135.0	1310.3	0.2	690.3	21.8	0.0	1.0	0.1	0.1	--	--	--
	2090	5531.4	2216.8	0.4	684.4	35.3	0.1	0.8	0.1	0.2	--	--	--
Outside Ham. Harb.	2097	4104.1	4781.1	1.2	646.6	183.7	0.3	0.2	0.4	2.0	--	--	--
Humber Bay	2113	11558.4	634.1	0.1	395.7	19.9	0.1	0.4	0.2	0.5	13.3	1.3	0.1
	2115	15738.2	327.1	0.0	438.7	13.4	0.0	1.3	0.1	0.1	14.5	3.5	0.2
	2118	9935.9	1114.6	0.1	292.4	21.0	0.1	0.6	0.3	0.5	7.4	0.7	0.1
	2330	7724.4	1115.9	0.1	242.9	16.5	0.1	0.4	0.2	0.5	--	--	--
	2331	7059.0	1369.0	0.2	248.1	9.6	0.0	0.4	0.2	0.5	--	--	--
	2334	2244.4	1303.8	0.6	181.1	30.3	0.2	0.2	0.2	1.0	--	--	--
	2335	5803.1	4730.5	0.8	168.5	92.3	0.5	0.1	0.4	4.0	--	--	--
	2368	5681.7	1015.3	0.2	196.1	12.9	0.1	0.3	0.1	0.3	--	--	--
	2370	9899.0	857.2	0.1	270.9	22.6	0.1	0.8	0.2	0.3	8.3	0.7	0.1
	2371	8068.5	772.1	0.1	438.7	18.7	0.0	0.2	0.1	0.5	6.6	1.0	0.2
Toronto Harbour	134a	4716.4	1647.6	0.3	142.4	14.3	0.1	0.6	0.2	0.3	--	--	--
	135a	13114.1	2132.6	0.2	391.2	40.3	0.1	0.3	0.3	1.0	--	--	--
	136a	8238.2	2778.3	0.3	227.6	11.5	0.1	0.4	0.4	1.0	--	--	--
	137a	8870.2	41655.7	4.7	180.6	30.6	0.2	0.3	0.2	0.7	--	--	--
	138a	8421.2	5136.4	0.6	227.9	39.0	0.2	0.1	0.5	5.0	--	--	--
	138b	7678.6	2657.2	0.3	425.8	32.9	0.1	0.3	0.3	1.0	--	--	--
	138c	7600.1	2358.2	0.3	381.5	9.3	0.0	0.3	0.3	1.0	--	--	--
	137b	8065.5	3441.4	0.4	203.3	28.8	0.1	0.1	0.3	3.0	--	--	--
	137c	4576.7	720.5	0.2	217.3	1.2	0.0	0.1	0.3	3.0	--	--	--
Eastern Headland	210b	4797.7	2341.4	0.5	325.7	68.8	0.2	0.1	0.2	2.0	6.0	0.8	0.1
	2277	10334.7	1622.2	0.2	403.2	44.0	0.1	0.3	0.4	1.3	11.6	1.8	0.2
	2281	9582.5	3260.3	0.3	458.6	50.0	0.1	0.1	0.4	4.0	5.3	3.6	0.7
	2284	11647.2	1839.1	0.2	442.2	17.4	0.0	0.4	0.5	1.3	--	--	--
	2273	6818.2	394.6	0.1	491.8	14.3	0.0	0.3	0.3	1.0	--	--	--
Ashbridges Bay	203d	3921.0	6117.3	1.6	83.8	72.5	0.9	0.8	0.2	0.2	--	--	--
E. Tor. Waterfront	2101	1631.8	790.2	0.5	121.5	7.5	0.1	0.1	0.1	1.0	--	--	--
	2102	1768.3	2136.6	1.2	171.3	6.0	0.0	0.4	0.4	1.0	--	--	--
	2103	2023.3	849.5	0.4	116.2	-0.6	0.0	0.1	0.1	1.0	--	--	--
	2082	1924.0	2997.1	1.6	136.9	24.6	0.2	0.2	0.2	1.0	--	--	--
	2083	2230.8	2403.3	1.1	159.1	34.5	0.2	0.1	0.2	2.0	--	--	--
St. Clair River	6c	5135.9	533.3	0.1	210.8	11.9	0.1	--	--	--	--	--	--
Niagara River	113	10725.2	9843.7	0.9	461.5	145.8	0.3	1.0	0.3	0.3	16.9	21.6	1.3
	157	8914.1	390.5	0.0	306.0	4.6	0.0	--	--	--	--	--	--
	160	3589.0	1416.8	0.4	123.1	22.4	0.2	--	--	--	--	--	--
	183	13339.0	23817.2	1.8	430.1	34.7	0.1	--	--	--	--	--	--
St. Marys River	45	6272.3	1030.2	0.2	64.9	39.6	0.6	0.1	0.5	5.0	--	--	--
	46	15043.8	256.2	0.0	197.1	12.0	0.1	0.6	0.3	0.5	34.3	18.0	0.5
	47	8549.2	715.1	0.1	128.0	8.5	0.1	0.4	0.1	0.3	--	--	--
	48	13280.3	104.2	0.0	362.4	-1.2#	0.0	0.6	0.0	0.0	--	--	--

-- No Data Available

See Text For Explanation Regarding Negative Values

BCF = Bioconcentration Factors (Contaminant concentration in benthic tissue/contaminant concentration in sediment

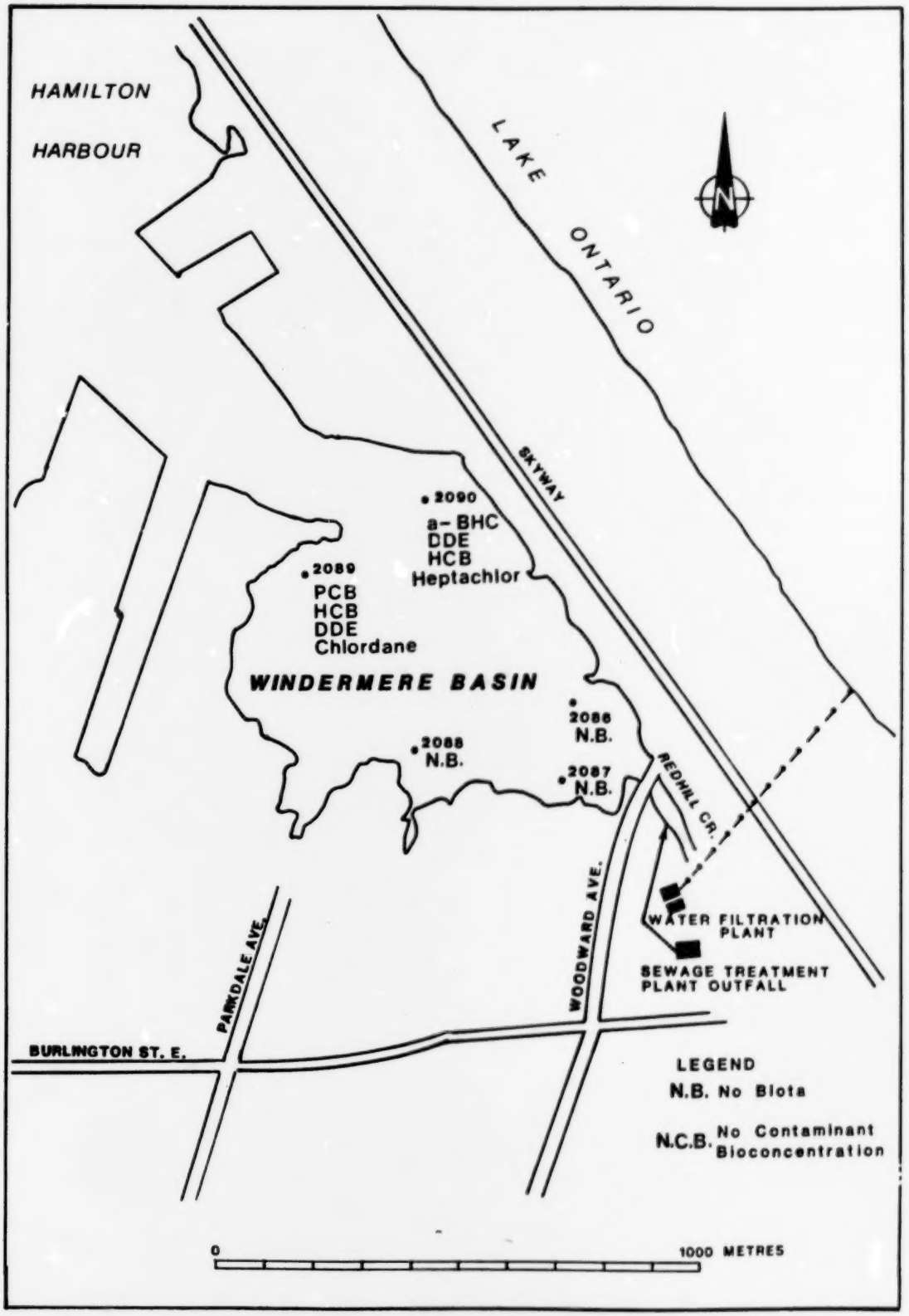

FIGURE 3.3a : WINDERMERE BASIN- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

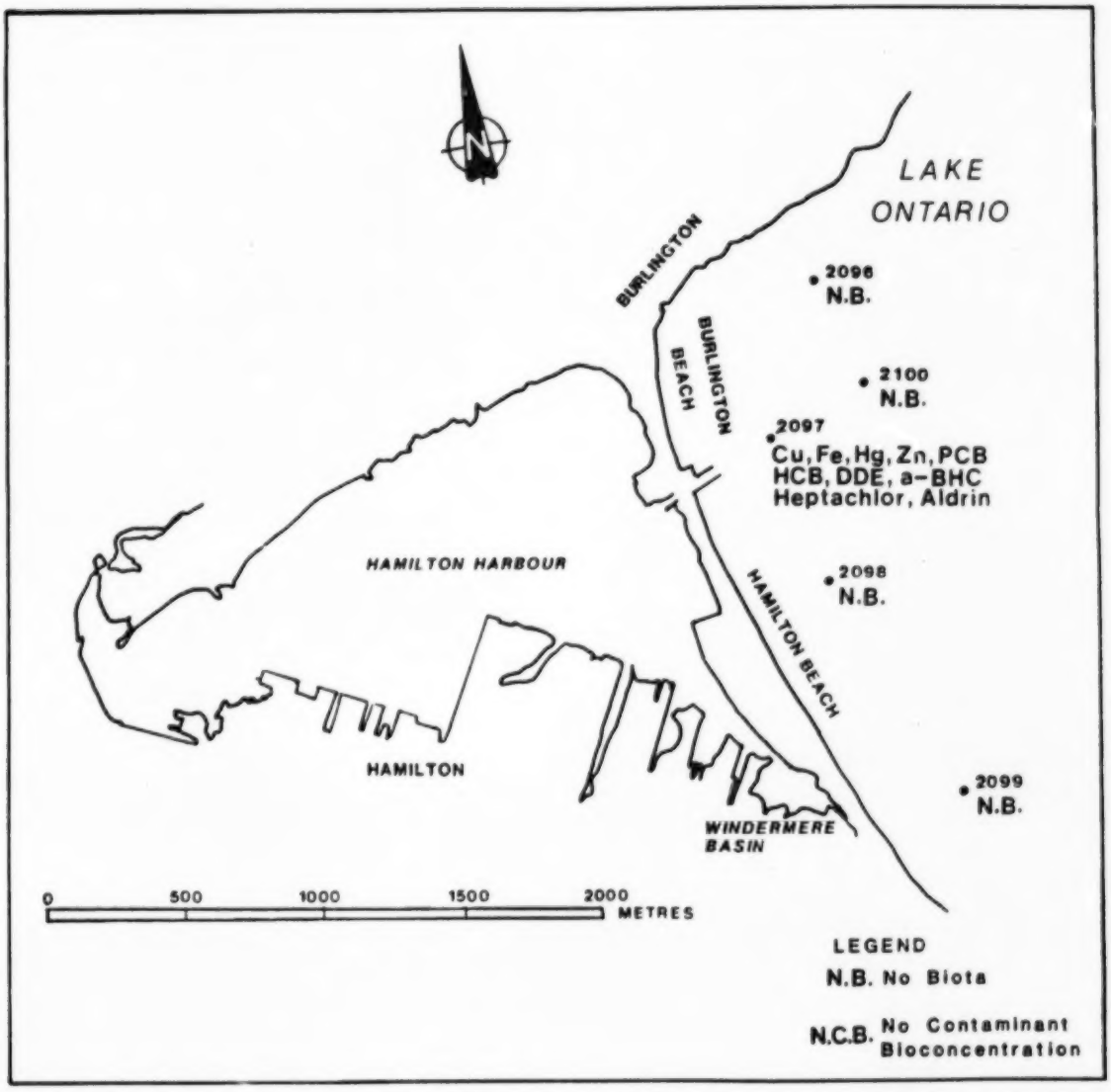

FIGURE 3.3b : OUTSIDE HAMILTON HARBOUR- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

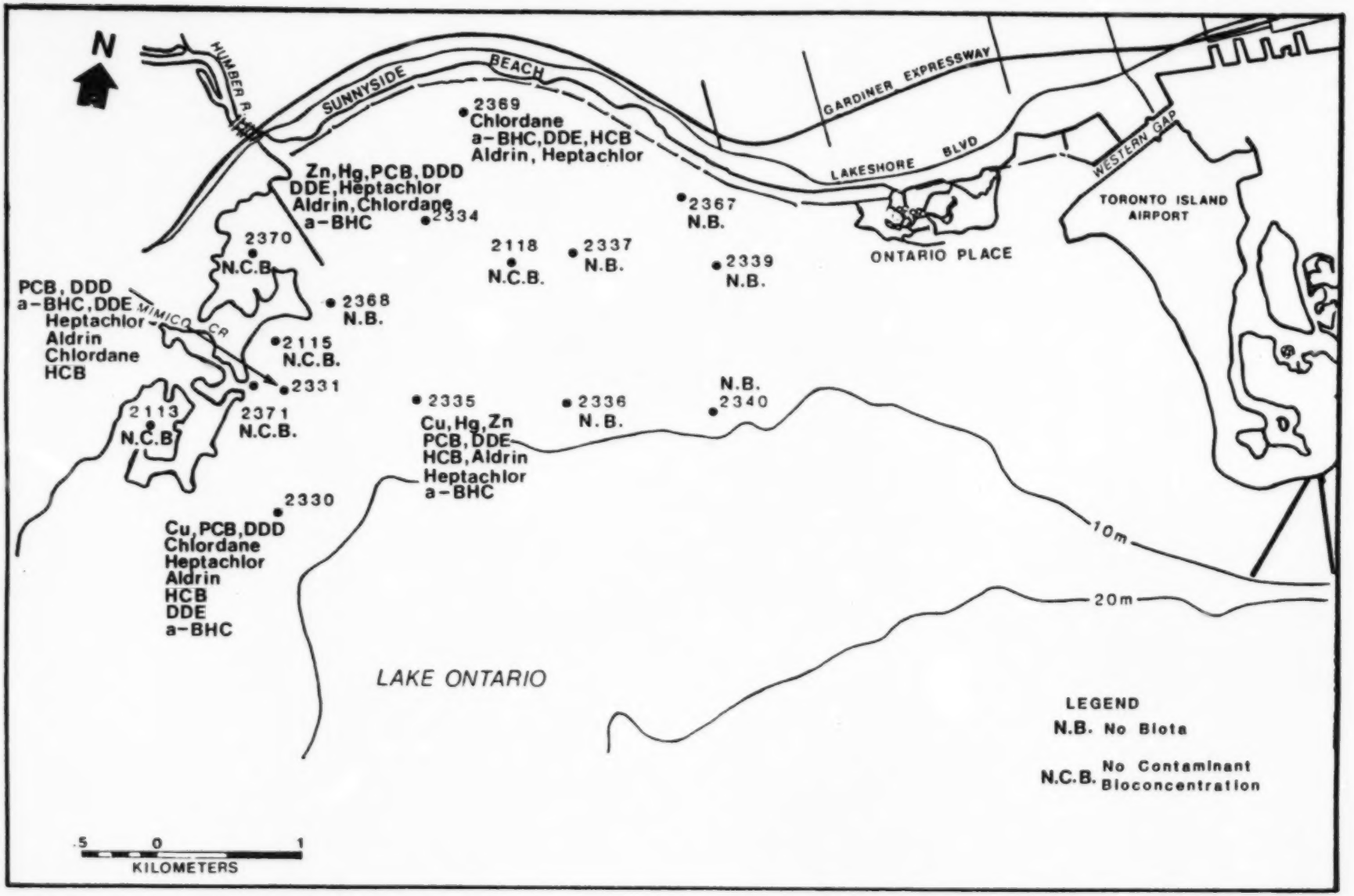

FIGURE 3.3c: HUMBER BAY- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

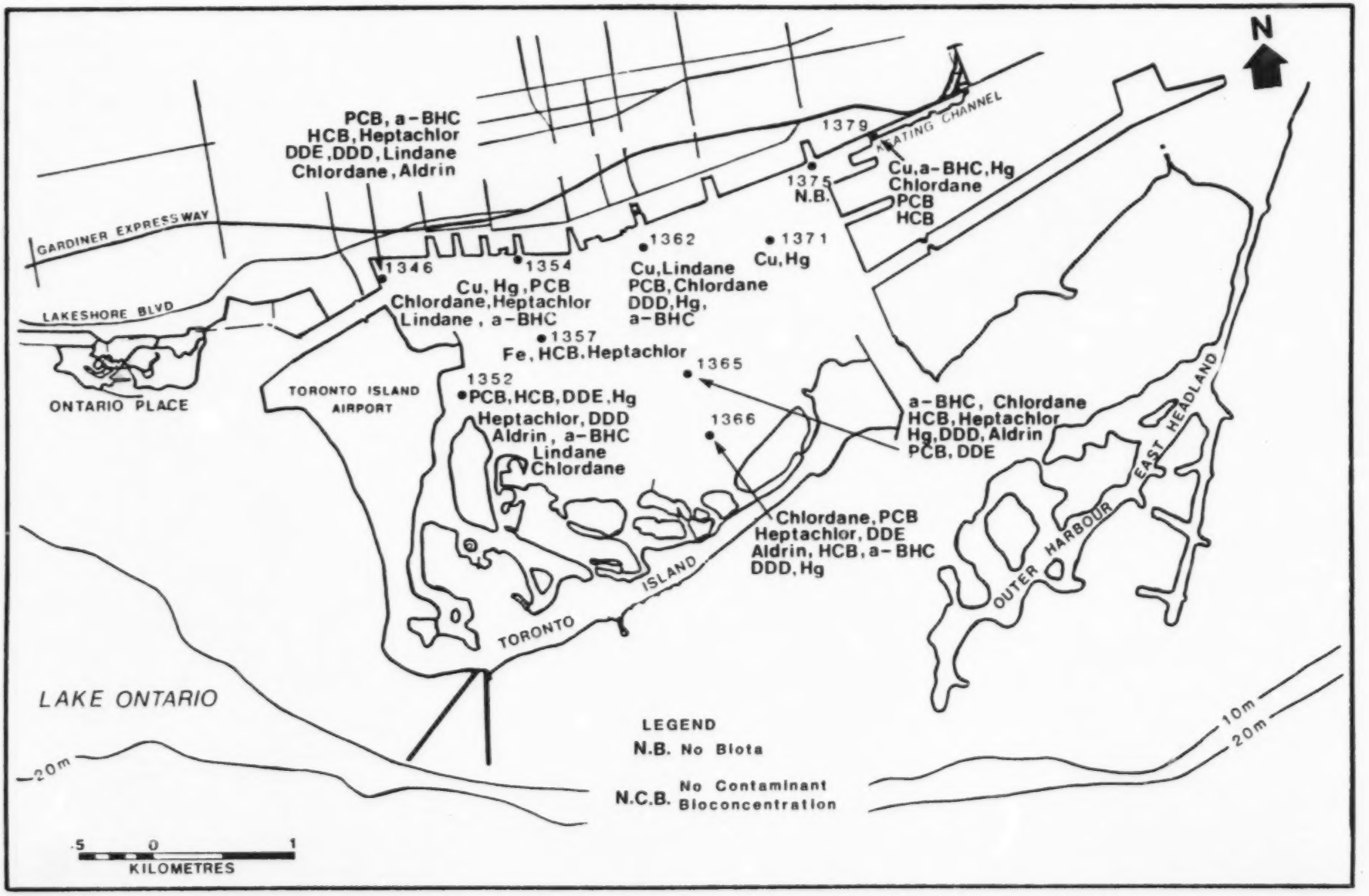

FIGURE 3.3d : TORONTO HARBOUR - STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

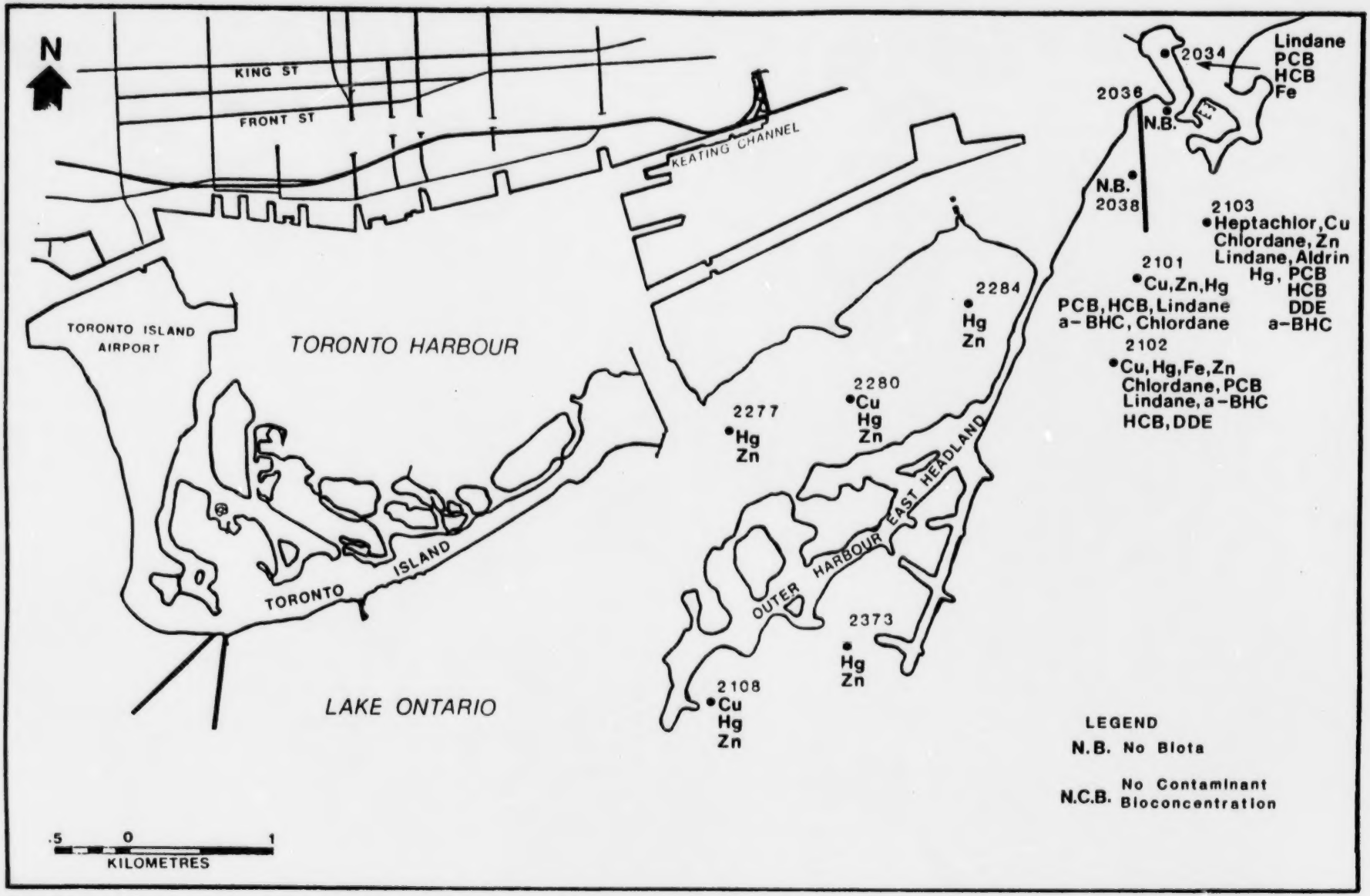

FIGURE 3.3e : EASTERN HEADLAND AND ASHBRIDGES BAY- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

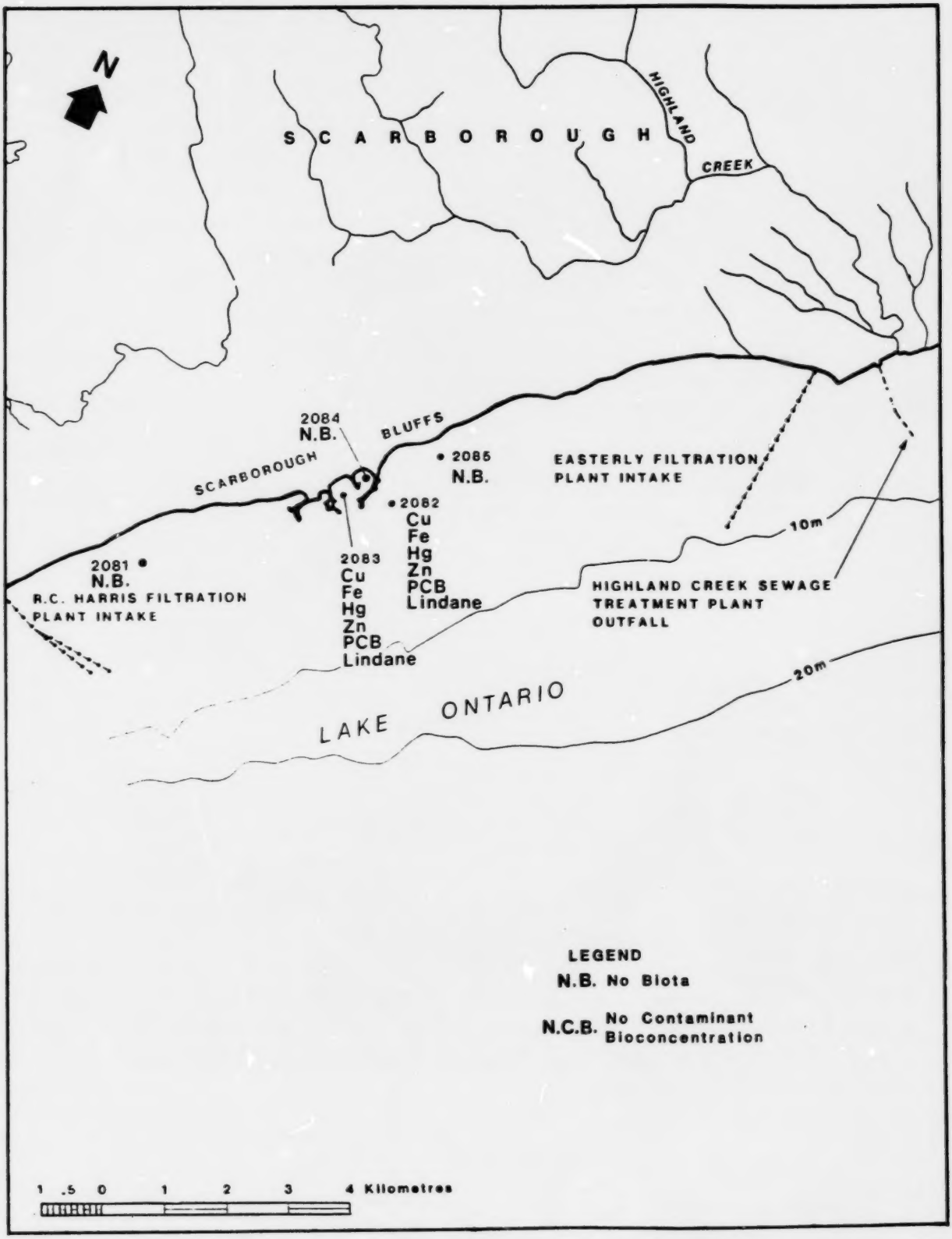

FIGURE 3.3f : SCARBOROUGH BLUFFS- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

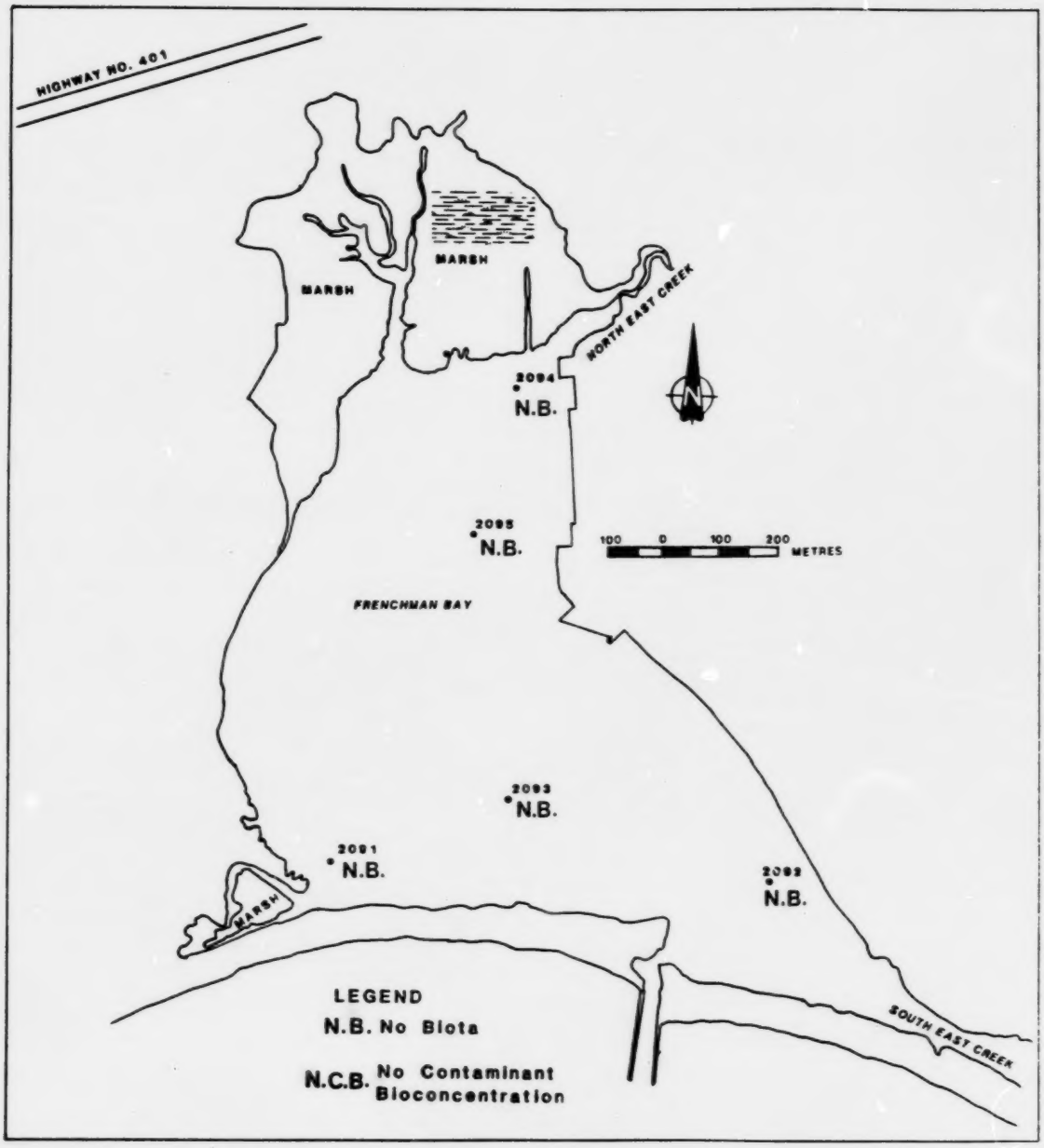

FIGURE 3.3g : FRENCHMAN BAY- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥ 1

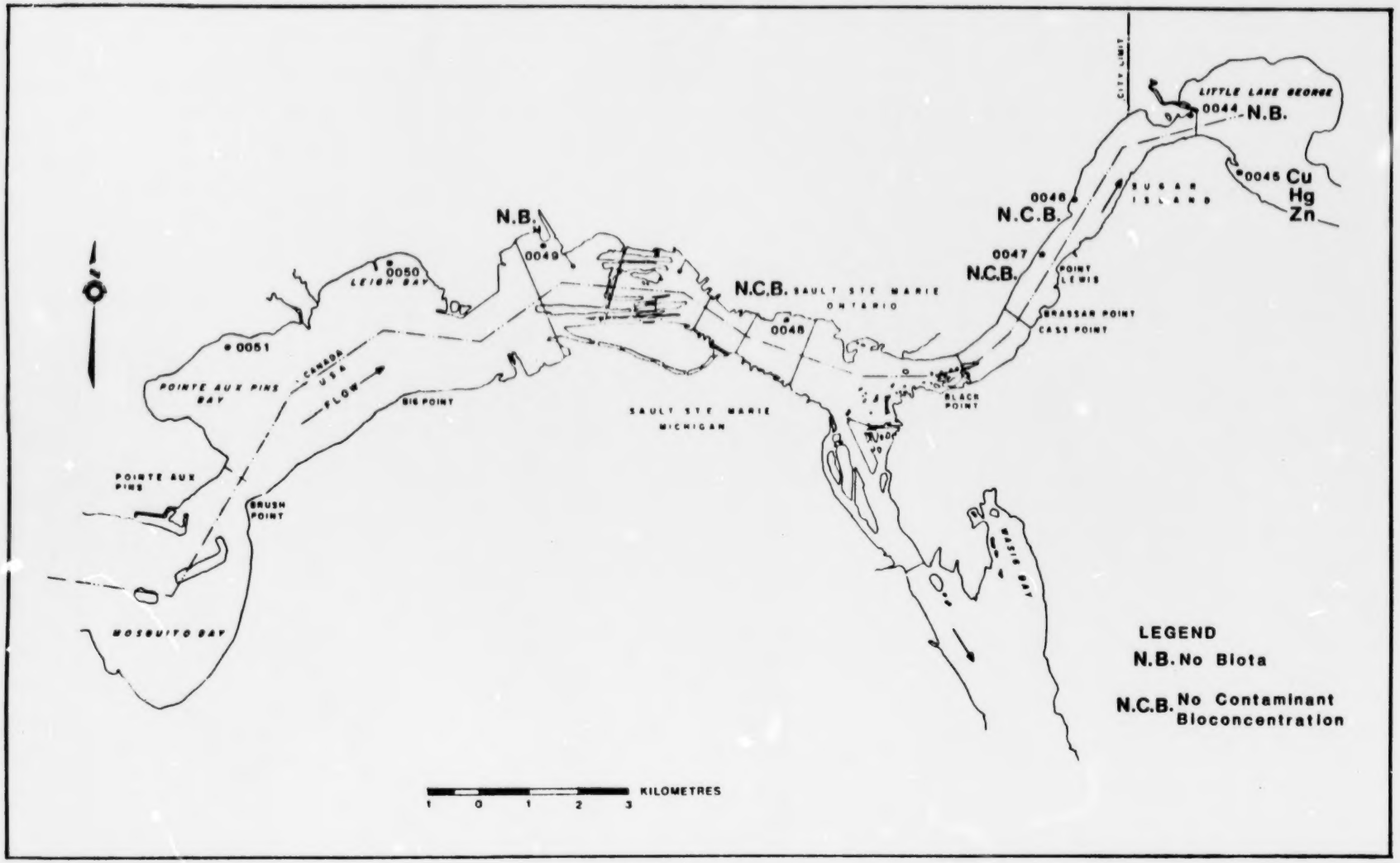

FIGURE 3.3h : ST. MARYS RIVER- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

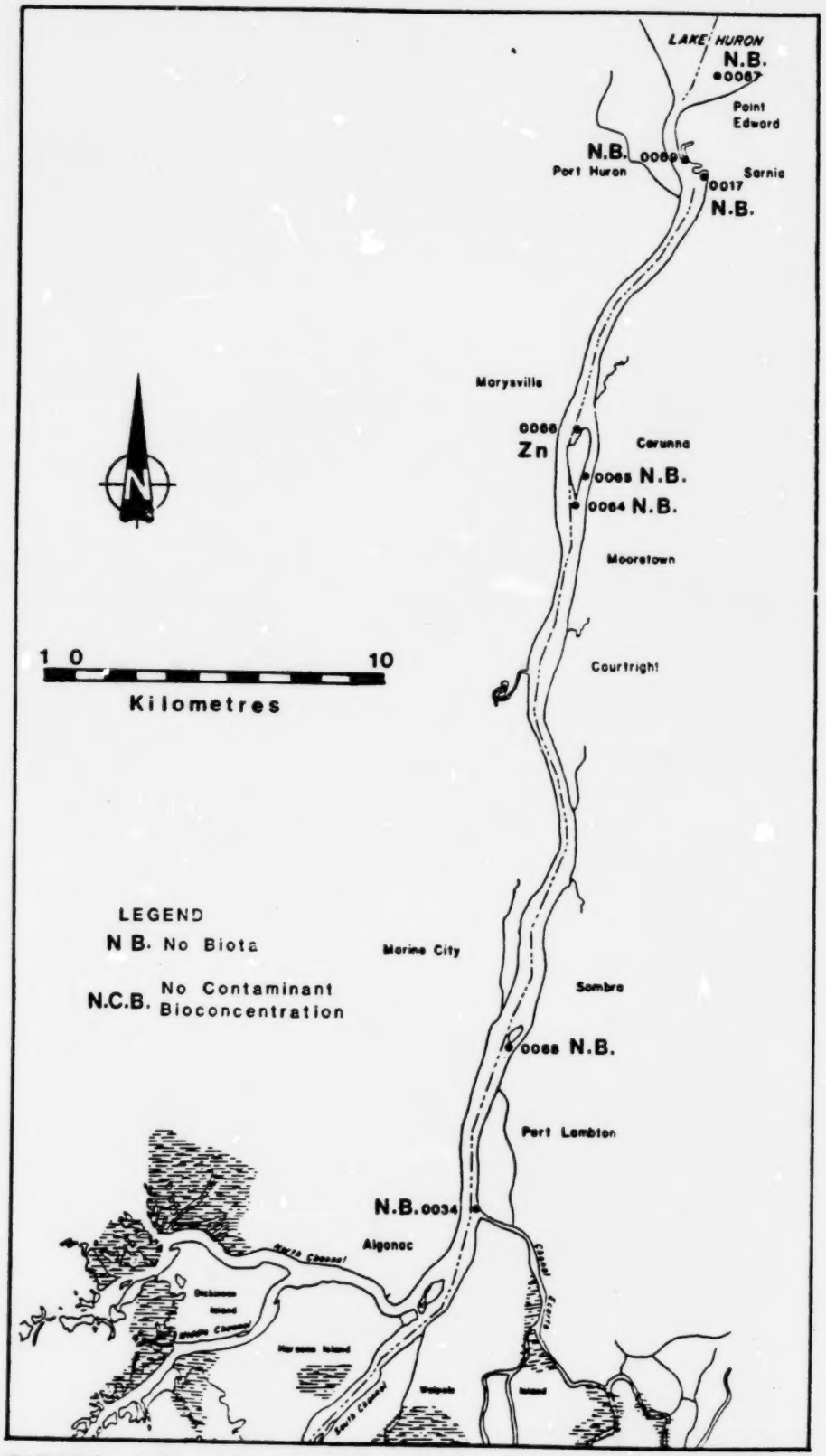

FIGURE 3.3i : ST. CLAIR RIVER- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

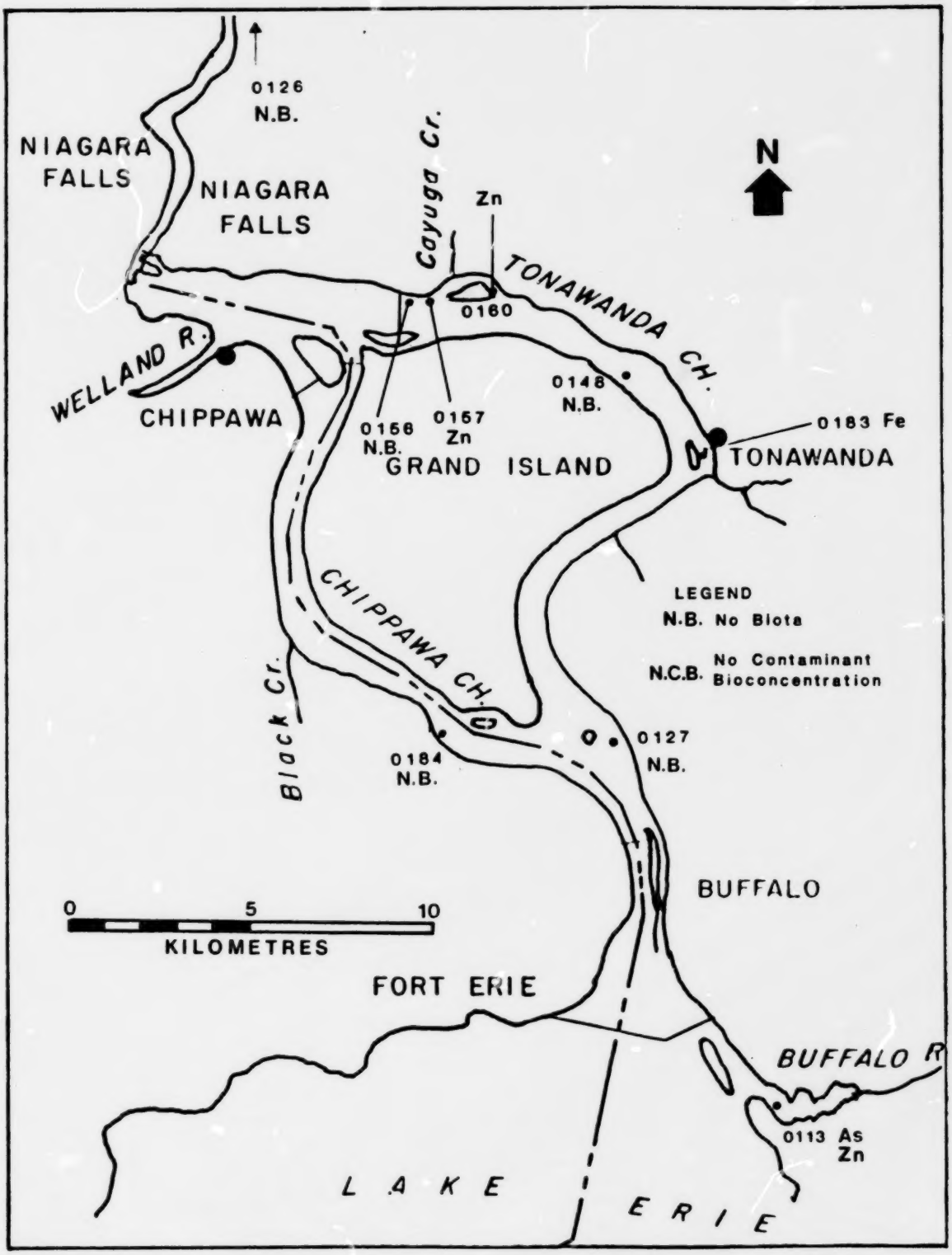

FIGURE 3.3j : NIAGARA RIVER- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

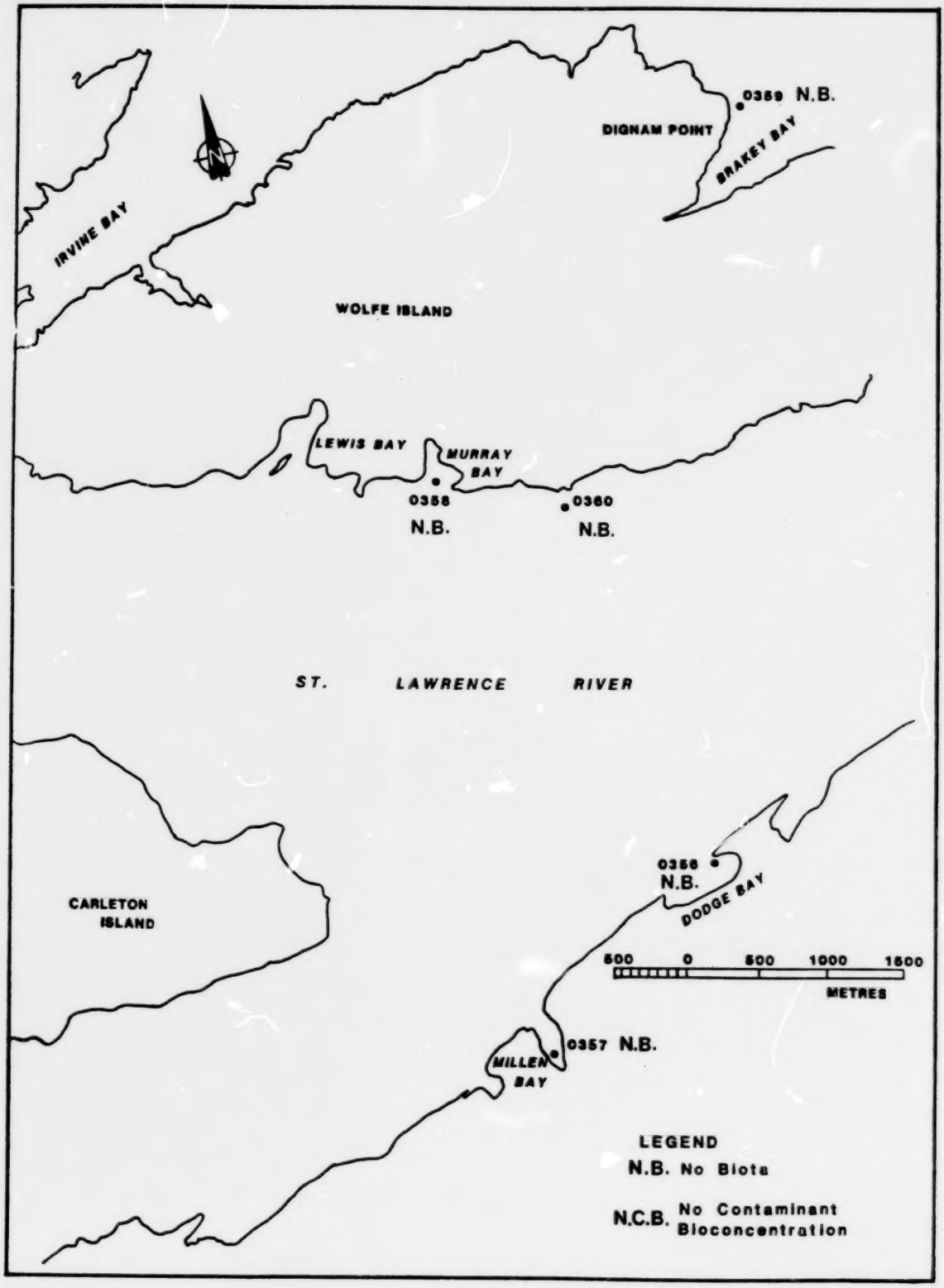

FIGURE 3.3k : ST. LAWRENCE RIVER- STATION LOCATIONS AND PARAMETERS SHOWING BIOCONCENTRATION FACTOR ≥1

showing body burden values of well over 100 ppm. The tissue concentrations were lower than iron but much higher than those of the other metals.

The body burden values of iron were generally lower than those of sediment, however, at 7 of the 42 stations, concentration factors of one or greater were noted. Most of these stations were located on the Toronto waterfront.

Mercury (Hg) in biota ranged from 0.07 ppm to 0.52 ppm and there appeared to be an upper limit to which mercury was concentrated in oligochaetes. Most of the values in organisms fell within the range of 0.2 to 0.5 ppm. Although the highest mercury concentrations in sediment were noted in the Niagara River, the organisms from this river showed very low uptake compared to most Toronto area stations.

3.3.2 Relationship Of Zinc And Copper In Biota To The Geochemical Phases Of Sediment.

The bioconcentration factors in Table 3.21 show 18 of the 42 stations for zinc and 15 of the 42 stations for copper with Zn and Cu levels in biota higher than those of the sediment. Among these, there were 10 common stations. Most of these stations were around the East Headland/Toronto Main STP. Four stations in Toronto Harbour showed Cu bioconcentration factors greater than one. Zinc values in biota were not elevated above sediment values in the harbour.

In general, with the exception of Hg, copper is the only metal that showed bioconcentration factors ≥1 in Toronto Harbour and this was limited to only the four stations referred to above. Most stations around the East Headland showed accumulation of Cu, Zn, and Hg by biota.

Forward stepwise regression analyses were carried out on the Zn and Cu sediment data from the respective stations with bioconcentration factors ≥1 in an attempt to identify parameters that may have an influence on body burden levels of these metals. The results are summarized in Table 3.22.

Table 3.22 RESULTS OF FORWARD STEPWISE*

REGRESSION ANALYSIS

Where Bioconcentration Factors $\geq$ 1 (Cu N = 16, Zn N = 17)

Dependent Variable :

Log Body Burden(dry weight, gut corrected concentrations in benthic tissue)

Zinc			Copper		
Independent Variables	Partial R^2	Probability	Independent Variables	Partial R^2	Probability
LOG F4(Zn)	0.47	$\leq$ 0.01	LOG F3(Cu)	0.67	$\leq$ 0.01
LOG LOI	0.43	< 0.02	EH	0.21	< 0.09
LOG SILT	0.28	< 0.06	LOG F1(Cu)	0.17	< 0.14
LOG F2(Zn)	0.17	< 0.16			
LOGMN	0.12	< 0.24			
ADJUSTED R SQUARED = 0.57			ADJUSTED R SQUARED = 0.61		
R SQUARED = 0.70			R SQUARED = 0.69		
MULTIPLE R = 0.84			MULTIPLE R = 0.83		

Zinc levels in biota appeared to be strongly related to the F4 phase of sediment (moderately reducible Fe/Mn oxyhydroxides) while Cu levels in biota showed a strong relationship to the F3 phase (organic/sulphide fraction) phase of sediment. Zinc levels in biota also showed a negative correlation with loss on ignition suggesting that Zn associated with organic matter may not be bioavailable.

4.0 DISCUSSION

4.1 Sediment Data

Contaminant levels in sediment showed considerable variation within and among the various study locations. High values for most parameters were noted in areas with industrial/municipal discharges such as Windermere Basin, Hamilton Harbour, Toronto Harbour, Humber Bay and St. Marys River. Among the Lake Ontario locations studied, Windermere Basin was the most contaminated area followed by Toronto Harbour and Humber Bay. The cleanest sediments were found along the Eastern Toronto Waterfront and at stations outside Hamilton Harbour. Among the rivers, St. Marys River had the highest levels of metals (except Hg) and solvent extractables which is perhaps due mainly to the large steel manufacturing industry discharging to the river. The sediments from the other rivers were much cleaner, approximating those of the Eastern Toronto Waterfront in quality. High levels of chromium were noted in Windermere Basin, Humber Bay and Toronto Harbour and is perhaps a reflection of high usage of this metal within large urban areas. The highest levels of mercury were noted in St. Clair and Niagara Rivers.

There were some distinctive variations in certain parameters among the areas sampled. Windermere Basin and Frenchman Bay showed high degree of organic enrichment. In Windermere Basin, this enrichment appears to be due mainly to solvent extractable type materials (oils and greases) whereas in Frenchman Bay, the sediments contain significant quantities of peat.

Organic pesticides were measured at very low concentrations in sediments and in many instances were below analytical detection limits.

Most chemical contaminants were associated with the fine-grained sediment (silt and clay particles). Strong correlations were noted between bulk chemical parameters in sediment and the organic content of the sediment, suggesting that the distribution pattern of the parameters is governed mainly by their association with organic material especially the solvent extractables (oils and greases). The strong relationship between metals and the organic content of sediments was supported by

findings from sequential extraction data which showed that the largest fraction of most metals (except Fe and Mn) was contained in the F3 phase (organic/sulphide). Iron was concentrated mainly in the residual phase and manganese was divided equally between the F3 and residual phases.

With the exception of Fe and to some extent Mn, most metals were in geochemically available forms (i.e. non-residual forms), which also suggested that a large fraction of the metals originated from anthropogenic sources.

The Fe and Mn oxyhydroxide fractions (F2 and F4) which have been reported in the literature (Forstner and Whittman, 1981) as important "carrier particles" of other metals, played very minor roles in comparison with the organic particles. The highest values of metals in the residual phase were noted consistently for sediments from the Eastern Toronto Waterfront. This area is exposed to the influence of waves and currents which minimize the deposition of fine-grained sediment. As a result, the substrate consists mainly of sandy material in which a significant proportion of the metals are inertly bound.

Based on the high degree of intercorrelation between parameters at the Toronto East Headland and in the St. Marys River, it appears that in addition to parameter association with fine-grained sediment, contaminant distribution is influenced by common sources in these respective areas. In the other areas sampled, the inter-relationships between parameters appear to be due mainly to their common association with organic "carrier particles" in sediment.

4.2 Biological Data

One of the basic assumptions in the design of the In-Place Pollutants Program was that there is a relationship between the levels of contaminants in benthic organisms and those of sediment since these organisms live in and process sediment for food. The two routes by which contaminants can be transferred from the environment to benthic tissue are through absorption from solution and from food sources (ie. transfer via the digestive process). The accumulation of metals in the

digestive glands of certain benthic organisms has been documented (Elder and Mattraw 1984, Newman and McIntosh, 1983) suggesting uptake via food sources and laboratory studies have demonstrated that benthic organisms can take up significant levels of PCB's directly from sediment (Meier and Rediske, 1984, Fowler et al., 1978). The study by Fowler, et al. examined the contribution of both water and sediment to PCB uptake by benthic worms and found that although uptake of PCB's from water was very rapid compared to uptake from sediment, the water route was of little importance because of the generally low levels of PCB in water compared to sediment concentrations. The study concluded that sediment was the more important of these two routes of uptake. The literature also reports several studies which showed significant uptake of contaminants from water by benthic organisms (Sanders and Chandler. 1972, Sodergren and Svenson, 1973, Marcelle and Thorme, 1984).

One of the important points that emerges from the literature is that when water contains appreciable concentrations of contaminants, especially the organochlorine contaminants (PCB/pesticides), it can represent the most significant source of contaminants to aquatic biota. With regards to benthic organisms under normal environmental conditions however, the importance of the water route is diminished because of the generally low levels at which organics such as PCBs are found in water compared with sediment (Fowler et. al., 1978).

Because of their wide geographic distribution and high population densities in Great Lakes sediments, most oligochaete studies have been centered on the Tubificid members especially T. tubifex and Limnodrilus spp. These organisms feed primarily on the top 2 to 8 cm of sediment, although they have been occasionally found at depths of 20 cm or more in sediment (McCall and Tevesz, 1982). The organisms feed with their heads down in the sediment and their posterior end exposed to the water immediately overlying the sediment (McCall and Tevesz, 1982). Respiration takes place predominantly (up to 90% in some cases - Brinkhurst and Jamieson, 1971) through the exposed tail region. This suggests that most contaminant uptake from solution will occur through the tail region and from the water column above the sediment - water interface as opposed to uptake from the interstitial water within the sediment matrix.

Tubificids feed selectively on the fine particles of sediment (silt and clays) and attached microflora such as bacteria (McCall and Tevesz, 1982). They pass large quantities of sediment through the gut and it is expected that some of the contaminants associated with the sediment will be absorbed by the organisms during digestion.

Information from the Phase 1 In-Place Pollutants study suggests that uptake from both sediment and bottom water may be important with regards to pesticides uptake by oligochaetes. At most of the stations sampled, the levels of pesticides in bottom sediments were extremely low but detectable levels were noted in the organisms at certain stations. Most of these stations were in the vicinity of discharge sources such as storm sewers and sewage treatment plant outfalls. A recent study (D. Boyd, 1987) investigated the levels of contaminants in suspended sediment at river mouths and in the final effluent at two sewage treatment plants in Toronto and found detectable levels of several pesticides in the suspended material. It appears that urban discharges represent sources of pesticides which are readily taken up by benthic organisms influenced by these discharges.

The organisms feeding on the upper sediment layers in the vicinity of these discharges may also take up contaminants from the aqueous phase during respiration since a proportion of recently discharged contaminants is likely to be present in the aqueous phase.

Once organic contaminants are in contact with sediment, the less persistent organics which include many of the organochlorine pesticides are readily degraded under anaerobic conditions (Muir and Yarechewski, 1984). The more persistent compounds such as PCBs are likely to become bound to organic matter or be dissolved in the solvent extractable fraction, which may render the contaminants unavailable. Laboratory studies have demonstrated that solvent extractables can significantly reduce the uptake of PCB's from sediments by benthic organisms (Meier and Rediske, 1984). Benthic organisms in contaminated sediments with high concentrations of solvent extractables and organic matter such as chitin and lignin (which are not easily degraded) are therefore, expected to show low levels of persistent organics such as PCBs. The data from the Phase 1 study showed that the oligochaetes obtained from

sediment with high organic content (measured as solvent extractables, loss on ignition and total organic carbon) generally had lower body burdens of Cu, Zn, Hg and PCBs compared with organisms from sediment with lower organic content (Table 4.1a-d) even though the concentrations of contaminants in the highly organic sediments were much greater. For Cu and Zn, sediments from stations with concentration factors less than one were more heavily contaminated with these metals compared to stations where concentration factors were one or greater. The data also showed very low uptake of Cd and Pb by benthic organisms. The literature suggests that Cd is not readily available to organisms under reducing conditions (Luoma, 1983). This may be one of the reasons for low Cd uptake, since most of the sediments sampled were anaerobic. Reasons for the low uptake of Pb are not readily apparent.

Information from the Phase 1 studies suggests that the tubificid members of the oligochaete can survive in sediments with relatively high levels of contamination. Other studies have shown that while tubificid worms, in particular T. tubifex and Limnodrilus spp. are tolerant of organic enrichment and anoxic sediment conditions that often accompany enrichment, these organisms are particularly intolerant of many chemical pollutants especially metals (Chapman et. al., 1982).

Findings similar to the Phase 1 In-Place Pollutants results were noted in a metal impacted lake in Indiana (Wentsel and McIntosh, 1977). The investigators in that study could not determine the mechanisms enabling the organisms to survive in sediments that were heavily contaminated with metals. Other studies (Bryan, 1975 and 1979) have shown that some species of benthic organisms can develop the capacity to survive under high metal pollution by previous exposure to sublethal levels. The tolerance developed through exposure to sublethal levels enabled the organisms to survive levels of pollution that would have been otherwise toxic. Laboratory studies have also shown that organisms from unpolluted areas that were not tolerant to Pb contamination could be made tolerant by exposure to sublethal levels of lead (Fraser, 1980). Fraser suggested that natural tolerance may be achieved by acclimation.

The ability of oligochaetes to survive in contaminated sediments and accumulate levels of various contaminants in their tissue raises concerns regarding the biological magnification of these chemicals in organisms that feed on the oligochaetes. This subject will be examined in another phase of the In-Place Pollutants Study.

** COPPER **

Table 4.1a Summary Statistics For The Distribution Of Copper In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

Copper In Sediment	Concentration Factors < 1 Median (N)	Range	Concentration Factors ≥ 1 Median (N)	Range
F3 Geochemical Fraction	83.11 (27)	(17.81-399.77)	18.99 (15)	(4.93-52.56)
Total Non-Residual (ΣIW-F4)	89.37 (27)	(18.63-427.64)	28.20 (15)	(11.12-56.60)
Copper In Biota				
Benthic Organisms	24.36 (27)	(9.60-77.30)	43.09 (15)	(15.60-82.00)
Organic Content In Sediment				
TOC (mg/g)	30.0 (11)	(12.0-68.0)	12.0 (11)	(0.1-37.0)
% LOI	7.0 (15)	(1.3-17.0)	3.3 (15)	(0.3-9.4)
Oil & Grease	4125.0 (15)	(920-24410)	1360.0 (15)	(360-9270)

(N) = Number of Stations

** ZINC **

Table 4.1b Summary Statistics For The Distribution Of Zinc In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 1 Median (N)	Range	Concentration Factors ≥ 1 Median (N)	Range
Zinc In Sediment				
F4 Geochemical Fraction	26.04 (24)	(3.15-885.81)	10.91 (18)	(0.16-64.83)
Total Non-Residual (IW-F4)	488.11 (24)	(249.66-2216.43)	109.25 (18)	(25.89-334.07)
Zinc In Biota				
Benthic Organisms	186.10 (24)	(71.80-283.00)	220.13 (18)	(62.90-663.40)
Organic Content In Sediment				
TOC (mg/g)	30.0 (15)	(12.0-68.0)	7.0 (7)	(0.1-22.0)
% LOI	7.8 (24)	(3.2-17.0)	2.1 (17)	(0.3-8.4)
Oil & Grease	5625.0 (24)	(1140.0-24410.0)	1230.0 (17)	(360.0-3550.0)

(N) = Number of Stations

** MERCURY **

Table 4.1c Summary Statistics For The Distribution Of Mercury In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 1		Concentration Factors ≥ 1	
	Median (N)	Range	Median (N)	Range
Hg in Sediment	0.60 (17)	(0.2-1.3)	0.16 (21)	(0.1-0.4)
Hg in Benthos	0.18 (17)	(0.1-0.3)	0.33 (21)	(0.1-0.5)
Organic Content in Sediment				
TOC mg/g	34.0 (8)	(12.0-68.0)	23.0 (14)	(0.1-37.0)
% LOI	7.0 (16)	(3.3-17.0)	3.7 (21)	(0.3-11.0)
Oil & Grease	6120.0 (16)	(1140.0-24410.0)	2150.0 (21)	(360.0-9270.0)

(N) = Number of Stations

** PCB **

Table 4.1d Summary Statistics For The Distribution Of PCB In Sediment And Benthic Tissue And The Organic Content Of Sediment According To Concentration Factors (all values in ug/g dry wt. unless stated otherwise)

	Concentration Factors < 10		Concentration Factors ≥ 10	
	Median (N)	Range	Median (N)	Range
PCB in Sediment	0.30 (12)	(0.03-3.09)	0.01 (10)	(0.01-0.12)
PCB in Benthos	1.24 (12)	(0.12-1.64)	1.34 (10)	(0.13-1.97)
Organic Content in Sediment				
TOC mg/g	31.0 (13)	(12.0-53.0)	5.0 (9)	(0.1-25.0)
% LOI	11.0 (13)	(3.3-17.0)	1.9 (9)	(0.3-5.4)
Oil & Grease	7610. (15)	(2900-24440)	870. (9)	(360-3550)

(N) = Number of Stations

5.0 CONCLUSION

One of the major objectives of the 1983 In-Place Pollutants Program was to obtain a good understanding of the relationship between contaminant levels in benthic organisms and those in the sediment that the organisms feed on. The data showed that such a relationship is a complex one, possibly involving various chemical, physico-chemical and physiological factors.

With regards to the uptake of contaminants by organisms, two trends were apparent. Several organochlorine pesticides were found at very low concentrations in sediment (many at the detection limits) but were elevated in benthic tissue at certain stations. Most of these stations were in the vicinity of storm sewers and sewage treatment plant discharges. Based on the results of other MOE studies (D. Boyd, 1987), indications are that low levels of these pesticides are discharged by these outfalls which provide the major source of uptake to benthic organisms. Once in contact with anaerobic sediment, these pesticides are readily degraded. The other trend is in relation to the other parameters, namely PCBs, Hg, Cu and Zn, which showed bioaccumulation. Here concentration by biota above sediment levels occurred in areas where the sediments had low organic matter content (measured as LOI, TOC, and SOL). There was no direct proportionality between the levels of these contaminants in sediment and benthic organisms and in the majority of cases, sediments with higher levels of these contaminants showed relatively low uptake by biota because of the correspondingly high levels of organic matter in these sediments.

The survival of benthic organisms in areas of relatively high levels of contamination and the concentration of certain contaminants in the tissue of these organisms raises concerns related to the potential for transfer of these contaminants to higher organisms that feed on these benthic species.

From a polluted sediment perspective, pesticides do not appear to be a major problem in contrast with urban storm sewers and sewage treatment

plant discharges. However, with regards to copper, zinc, PCBs and mercury, the sediments appear to be the major source of uptake by benthic organisms.

The sequential extraction procedure used in assessing the geochemical distribution of metals in sediment provides useful information on potential availability and the fraction(s) that influence body burden. The actual amounts of metals released from sediment may not necessarily be equivalent to the amounts potentially available because of physico-chemical factors and the amounts of organic matter in sediments.

Contaminated sediment is a source of contaminants to benthic organisms and can exert toxic influences on benthic organisms by completely eliminating benthic populations or reducing the diversity to a few tolerant species. The effects of continuing discharges such as storm sewers and STP discharges cannot however, be overlooked, since they are still of major concern in areas with contaminated sediment. Any management strategy to improve sediment quality must first address input from these sources.

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